THE ORIGIN OF SPECTRA

BY

PAUL D. FOOTE
Physicist, U. S. Bureau of Standards

AND

F. L. MOHLER
Physicist, U. S. Bureau of Standards

-8 FEB 2008

AGRICULTURAL COLLEGE AND RESEARCH INSTITUTE
No. 122
10 JUN 1924
COIMBATORE

American Chemical Society

BOOK DEPARTMENT

The CHEMICAL CATALOG COMPANY *Inc.*
19 EAST 24TH STREET, NEW YORK, U. S. A.
1922

Copyright, 1922, By
The CHEMICAL CATALOG COMPANY, *Inc.*
All Rights Reserved

Press of
J. J. Little & Ives Company
New York, U. S. A.

GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is

difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of

the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

AMERICAN CHEMICAL SOCIETY

BOARD OF EDITORS

Scientific Series:—
William A. Noyes, *Editor*,
Gilbert N. Lewis,
Lafayette B. Mendel,
Arthur A. Noyes,
Julius Stieglitz

Technologic Series:—
John Johnston, *Editor*,
C. G. Derick,
William Hoskins,
F. A. Lidbury,
Arthur D. Little,
C. L. Reese,
C. P. Townsend.

American Chemical Society

MONOGRAPH SERIES

Other monographs in the series of which this book is a part now ready or in process of being printed or written.

Organic Compounds of Mercury.
By Frank C. Whitmore. 397 pages. Price $4.50.
Industrial Hydrogen.
By Hugh S. Taylor. 210 pages. Price $3.50.
The Chemistry of Enzyme Actions.
By K. George Falk. 140 pages. Price $2.50.
The Vitamins.
By H. C. Sherman and S. L. Smith. 273 pages. Price $4.00.
The Chemical Effects of Alpha Particles and Electrons.
By Samuel C. Lind. 180 pages. Price $3.00.
Zirconium and Its Compounds.
By F. P. Venable. Price $2.50.
The Properties of Electrically Conducting Systems.
By Charles A. Kraus. Price $4.50.
Carotinoids and Related Pigments: The Chromolipoids.
By Leroy S. Palmer. About 200 pages, illustrated.
Thyroxin. By E. C. Kendall.
The Properties of Silica and the Silicates. By Robert B. Sosman.
Coal Carbonization. By Horace C. Porter.
The Corrosion of Alloys. By C. G. Fink.
Piezo-Chemistry. By L. H. Adams.
Cyanamide. By Joseph M. Braham.
Ammonia Compounds. By E. C. Franklin.
Wood Distillation. By L. F. Hawley.
Solubility. By Joel H. Hildebrand.
Glue and Gelatin. By Jerome Alexander.
Organic Arsenical Compounds. By George W. Raiziss. Jos. L. Gavron.
Valence, and the Structure of Atoms and Molecules. By Gilbert N. Lewis.
Shale Oil. By Ralph H. McKee.
Aluminothermic Reduction of Metals. By B. D. Saklatwalla.
The Analysis of Rubber. By John B. Tuttle.
The Chemistry of Leather Manufacture. By John A. Wilson.
Absorption Carbon. By N. K. Chaney.
Refining Petroleum. By George A. Burrell, *et al.*
Extraction of Gasoline from Natural Gas. By George A. Burrell.

The CHEMICAL CATALOG COMPANY, *Inc.*
19 EAST 24TH STREET, NEW YORK, U. S. A.

PREFACE

Although several accounts of the quantum theory of spectra from the mathematical standpoint have appeared in the past year, the experimental aspect of the problem has been greatly subordinated.

In this book the authors have endeavored to present the subject from the experimental side. However, in order to do this, it was found necessary to briefly discuss the theoretical developments. In this regard, the important assumptions involved are enumerated, and only the essential steps in the mathematical analysis are presented. The reader will find the detailed mathematical treatment in the papers given as references, especially in the works of Bohr and Sommerfeld.

The experimental phase of the quantum hypothesis as applied to spectroscopy was given its first impetus by the pioneer work of J. Franck whose later important researches have contributed much to the development of the subject. The theoretical deductions of Sommerfeld on fine structure have been beautifully verified by the precision spectroscopic work of Paschen. The most recent contributions of Bohr on atomic structure have removed many of the objections of the chemist to the physicist's conception of a planetary structure with revolving electrons. At the same time Bohr's viewpoint has necessitated the revision of some of the conceptions of the physicist.

The subject matter is recognizedly in a transitional stage and the theoretical interpretation of experimental phenomena here given is in no sense complete or final. However, the experimental facts will remain and no time is more opportune for their systematic correlation than the present moment.

This book is incomplete in many respects. For example, consideration of the extensive experiments on the Stark and Zeeman effects and on band spectra has been omitted, in part because their adequate treatment seemed to require more space than was deemed advisable to devote to these subjects, and in part because of the authors' inexperience in these fields of spectroscopy.

The title of the book was suggested by a lecture of Prof. J. C. McLennan whose many experiments in this field of physics are considered in the text.

The authors desire to acknowledge the helpful coöperation and advice of their colleague Dr. W. F. Meggers. Many of their experiments have been undertaken with Dr. Meggers as co-worker and he has very kindly prepared most of the photographic prints of spectra reproduced here as half-tones. Dr. K. T. Compton furnished the advance manuscript of his paper on Cumulative Ionization, a synopsis of which is given in Chapter VI. Dr. R. C. Tolman, Dr. C. A. Skinner and Mr. Arthur E. Ruark have very generously given much of their time in reading the manuscript, and have offered many suggestions which have been incorporated in the text.

The authors wish to express their appreciation of the interest with which the late Dr. C. W. Waidner, former Chief of the Heat Division of this Bureau, followed the course of their work until within a few days of his death. The authors also desire to thank Dr. S. W. Stratton for placing at their disposal every means and facility which could advance their own experimental work in this subject. And finally, the authors are especially grateful to the Monograph Committee of the American Chemical Society, its Chairman, Prof. W. A. Noyes, and Prof. A. A. Noyes, for making possible the publication of this volume.

P. D. F.

Bureau of Standards, May 22, 1922. F. L. M.

TITLES OF CHAPTERS

CHAPTER		PAGE
I.	The Quantum Theory of Spectroscopy	15
II.	Energy Diagrams	51
III.	Ionization and Resonance Potentials for the Elements	60
IV.	Line Absorption Spectra of Atoms	78
V.	Line Emission Spectra of Atoms	109
VI.	Cumulative Ionization	148
VII.	Thermal Excitation	157
VIII.	Thermochemical Relations	177
IX.	X-Ray Spectra	192
X.	Photo-Electric Effect in Vapors	216
XI.	Determinations of h Involving Line Spectra	223

APPENDICES

APPENDIX		
I.	Computational Data	227
	Periodic Table	231
II.	Bohr's Theory of Atomic Structure	232
	Index of Subjects	243
	Index of Authors	249

TABLE OF CONTENTS

CHAPTER		PAGE
I.	THE QUANTUM THEORY OF SPECTROSCOPY	15
	The Simple Theory of Hydrogen and Ionized Helium	16
	Ratio of Mass of Hydrogen Nucleus and Hydrogen Atom to Mass of Electron, and Value of e/m	18
	Elliptical Orbits	19
	Relativity of Mass	24
	The Principle of Selection	26
	Experimental Verification by Fine Structure Analysis	27
	Atoms with Many Electrons	30
	Derivation of the Ritz Equation	32
	Application of the Ritz Equation	34
	Fine Structure, Doublets and Triplets	37
	Nuclear Defect of a Ring of Electrons	37
	Spark Spectra	39
	Spectroscopic Tables	43
	X-Rays	46
II.	ENERGY DIAGRAMS	51
III.	IONIZATION AND RESONANCE POTENTIALS FOR THE ELEMENTS	60
	Group I	63
	Group II	63
	Group III	63
	Group IV, Group V	65
	Group VI	66
	Group VII, Groups VIII and 0	67
	Hydrogen	68
	The Normal Helium Atom	69
	The Hydrogen Molecule	74
IV.	LINE ABSORPTION SPECTRA OF ATOMS	78
	Line Absorption Spectra of Normal Atoms	78
	Reversed Lines	82
	Resonance Radiation	86
	The Broadening of Spectral Lines	91
	Doppler Effect	91
	Impact Damping	92
	Line Absorption Spectra of Excited Atoms	93
	The Measurement of τ (the life of an excited atom)	93
	Absorption of Subordinate Series Lines	97

CHAPTER		PAGE
V.	LINE EMISSION SPECTRA OF ATOMS	109
	Metals of Group II of the Periodic Table	118
	Relation between 1 𝔖 and 1 *S*	124
	Metals of Group I of the Periodic Table	127
	The Rare Gases	133
	Helium	133
	Neon	136
	Franck and Einsporn's Observations onMercury	137
	Quantitative Spectroscopic Analysis in its Relation to the Origin of Spectra	141
	Long Lines	141
	Raies Ultimes	141
VI.	CUMULATIVE IONIZATION	148
	Excitation by Electronic Impact	149
	Excitation by Absorption of Radiation	150
	Numerical Magnitudes	152
	Arcs below the Ionization Potential	153
	Ionization by Successive Photo-Electric Action	154
	Further Conclusions	155
VII.	THERMAL EXCITATION	157
	Thermodynamic Considerations	157
	Simple Ionization	159
	Double Ionization	161
	Thermal Excitation without Ionization	163
	Flame Spectra	165
	Spectral Lines Correlated with Temperature	169
	Solar Spectra	170
	Stellar Spectra	172
VIII.	THERMOCHEMICAL RELATIONS	177
	Electron Affinity of Atoms	177
	Grating Energy, Ionization Potential and Electron Affinity	179
	Ionization of Vapors of Compounds	184
	Critical Potentials and Radiation from Elements in the Polyatomic State	187
IX.	X-RAY SPECTRA	192
	Introduction	192
	Critical Potentials for X-Ray Excitation	193
	Absorption Phenomena	196
	Emission Lines and the Combination Principle	204
	Theoretical Significance of the System of Absorption Limits	209
	Conclusion	213

CHAPTER PAGE
X. Photo-Electric Effect in Vapors 216

XI. Determinations of *h* Involving Line Spectra . . 223
Characteristic X-Rays 223
The Rydberg Number 224
Ionization and Resonance Potentials 225

Appendix I 227
Computational Data 227
Nuclear Defect, Table 44 227
Numerical Magnitudes, Table 45 228
Velocities of Electrons, Ions and Molecules 229
Periodic Classification of Elements, Table 46 . . . 231

Appendix II. Bohr's Theory of Atomic Structure . . . 232
1st Period 233
2nd Period 235
3rd, 4th and 5th Periods 235
6th and 7th Periods 235
X-Ray Spectra 237
Superficial Atomic Properties 237
Arc and Spark Spectra 239
Conclusion 240

Index of Subjects 243

Index of Authors 249

1228
10 JUN 1924
CULTURAL INSTITUTE LIBRARY
COIMBATORE

Chapter I

The Quantum Theory of Spectroscopy

The quantum theory of spectra has been concerned mainly with the Rutherford type of atom. This consists of a positive nuclear charge Ze, where Z is the atomic number, surrounded by Z electrons. Practically the entire mass of the atom is concentrated in the positive core, the size of which, however, is much smaller than that of an electron.[1] The electrons are usually considered as revolving about the nucleus in coplanar orbits. Actually there is evidence that the orbits are not coplanar and models have been proposed in which the electrons do not revolve about the nucleus, but with the exception of helium little progress from the quantitative, spectroscopic and mathematical standpoints has been made with such types of atom.

Even if we really understood the precise structure of a heavy atom, the mathematical analysis of the orbits would be hopeless — a problem of n bodies where n is large. Hence the exact interpretation of spectroscopic phenomena is a problem for the far-distant future. For the present bold simplifying assumptions must needs be made for the purpose of obtaining results. Postulates are proposed, the only apparent justification of which lies in the applicability of the conclusions to experimental facts. When necessary, the fundamental principles of classical dynamics are temporarily abandoned and apparently illogically accepted for later steps in the analysis of the problem. In spite of such inconsistency the quantum theory of spectra is the only satisfactory attempt so far made toward interpreting spectral series and, already, by predictions from theory, has led to experimental verifications of the greatest moment. This is the goal of any theory; not necessarily to explain nature but to aid in a systematic search for new phenomena.

[1] The mass is of electromagnetic nature. As appears later, the ratio of the mass of the hydrogen nucleus to that of a slow-moving electron is about 1846. Since the diameter of a spherical charge is inversely proportional to its mass, the hydrogen nucleus should have 1/1846 the diameter of an electron. The best guess is probably 10^{-16} cm for the diameter of this nucleus, but any estimate involves questionable conjectures.

THE SIMPLE THEORY OF HYDROGEN AND IONIZED HELIUM

We shall first consider simple atoms containing the nucleus and a single electron. Such an atom is hydrogen, ionized helium, or doubly ionized lithium. Merely by way of introduction we shall postulate that the electron of charge $-e$ for hydrogen revolves in a circular orbit about the nucleus of charge $+e$. Since the mass of the electron is small compared to that of the nucleus, we may readily derive from simple mechanics the total energy W of the revolving electron (the sum of the kinetic and potential energies).

$$W = -\frac{e^2}{2a}, \qquad \frac{1}{a} = \frac{mv^2}{e^2}, \tag{1}$$

where a is the radius of the circular orbit, m the mass of the electron and v its linear velocity.

So far as ordinary mechanics is concerned a may have any value whatever, depending upon "initial conditions". Bohr,[2] however, postulates that only certain definite sizes of orbits are permissible stationary states, so determined that

$$2\pi \times \text{angular momentum} = nh, \tag{2}$$

where h is Planck's universal constant of action and n may assume integral values only. Whence:

$$2\pi mav = nh.$$

Substituting this in the relation $ma^2v^2 = -e^4/2W$ obtained from (1) we find for W_n the total energy of the electron in the nth orbit:

$$W_n = -\frac{2\pi^2 me^4}{h^2}\frac{1}{n^2}. \tag{3}$$

In order for this to be a stationary state, no energy can be radiated. On the basis of classical dynamics, however, an accelerated electron emits radiation and hence the electron should spiral in toward the nucleus instead of remaining in the nth orbit. We accordingly *postulate* that on the basis of the quantum theory the nth orbit is a stationary state and that no energy is radiated so long as the electron remains in this orbit. If, however, it should jump to the n'th orbit Bohr further postulates that radiation is suddenly emitted of such frequency $\bar{\nu}$ that

$$W_n - W_{n'} = h\bar{\nu}. \tag{4}$$

The quantity $h\bar{\nu}$ is known as a quantum of energy of frequency $\bar{\nu}$. Hence in any interorbital transition a single quantum of radiation is

[2] See general reference 1 at end of chapter.

emitted ($n > n'$) or absorbed ($n < n'$), the magnitude of which (expressed in ergs for example) is equivalent to the difference in total energies of the electron in the two orbits concerned. This fact is simply an application of the principle of the conservation of energy. Substituting the values of W from Equation (3) in the above, we obtain:

$$\bar{\nu} = \frac{2\pi^2 me^4}{h^3}\left[\frac{1}{n'^2} - \frac{1}{n^2}\right]. \qquad (5)$$

In general it is desirable to express our values in terms of wave number ν, *i.e.* the reciprocal of the wave-length in cm in vacuo. Whence, since $\nu = \bar{\nu}/c$ where c is the velocity of light:

$$\nu = N\left(\frac{1}{n'^2} - \frac{1}{n^2}\right), \qquad (6)$$

in which

$$N = \frac{2\pi^2 me^4}{ch^3} = N_\infty. \qquad (7)$$

The subscript ∞ is sometimes added to call attention to the fact that we have assumed the mass of the electron as negligible compared to that of the core. Formula (6) gives to a high degree of precision all the series lines of the hydrogen atom. With $n' = 1, n = 2, 3$, etc., we have the Lyman ultra-violet series; with $n' = 2$, $n = 3$, 4, etc., the Balmer series; and with $n' = 3$, $n = 4$, the Paschen series of infra-red lines.

If we consider the effect[3] of the finite mass M of the nucleus we find that the constant N in (6) must be replaced by:

$$N_{\mathrm{H}} = \frac{M}{m + M}N_\infty. \qquad (8)$$

This is appreciably different from N_∞ for hydrogen as well as for other light elements. The observed value of N_{H} obtained from an empirical consideration of the series lines agrees well with that computed by (8) and (7) from the known physical constants m, e, c and h. For ionized helium we may derive in the above manner:

$$\nu = 4\,N_{\mathrm{He}}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right). \qquad (9)$$

The factor 4 enters because of the nuclear charge $Z = 2$ which occurs in the derivation as Z^2. This formula again represents important series lines, formerly attributed to hydrogen but now known to be due to ionized helium, for example the series $n' = 3$, $n = 4$, 5, etc., also $n' = 4$, $n = 5$, 6, etc.

[3] Both nucleus and electron revolve around the common center of mass. In this and following developments we are concerned with the energy, momentum, etc., of the entire system, not of the electron alone. The substitution of $\frac{Mm}{m + M}$ for m in the above equations takes account of this.

Ratio of Mass of Hydrogen Nucleus and Hydrogen Atom to Mass of Electron, and Value of e/m

From empirically determined values of N_{H} and N_{He} it is possible to obtain the ratio of the mass of the hydrogen atom to that of an electron. Paschen finds empirically:

$$\left.\begin{aligned} N_{\text{H}} &= 109677.691 \\ N_{\text{He}} &= 109722.144 \\ \text{and through Equation (8)} \quad N_{\infty} &= 109737.11 \end{aligned}\right\} \qquad (10)$$

$$\frac{\text{mass of helium atom}}{\text{mass of hydrogen atom}} = \frac{M'_{\text{He}}}{M'_{\text{H}}} = \frac{4.00}{1.0077} = 3.969,$$

from atomic weight determinations.

Let
$$\frac{\text{mass of helium nucleus}}{\text{mass of hydrogen nucleus}} = \frac{M_{\text{He}}}{M_{\text{H}}} = x.$$

From Equation (8) it follows that:

$$\frac{M_{\text{H}}}{m} = \frac{\text{mass of hydrogen nucleus}}{\text{mass of slow-moving electron}} = \frac{N_{\text{H}} - \frac{1}{x}N_{\text{He}}}{N_{\text{He}} - N_{\text{H}}} \qquad (11)$$

But
$$\frac{M'_{\text{He}}}{M'_{\text{H}}} = \frac{M_{\text{He}} + 2\,m}{M_{\text{H}} + m} = 3.969.$$

Hence
$$x = 1.969\frac{m}{M_{\text{H}}} + 3.969.$$

Assume $1900 > \frac{M_{\text{H}}}{m} > 1800$. Then $x = 3.970$.

Accordingly, from Equations (10) and (11),

$$\frac{M_{\text{H}}}{m} = \frac{\text{mass of hydrogen nucleus}}{\text{mass of slow-moving electron}} = 1845.5.$$

And
$$\frac{M'_{\text{H}}}{m} = \frac{\text{mass of hydrogen atom}}{\text{mass of slow-moving electron}} = \frac{M_{\text{H}} + m}{m} = 1846.5.$$

This value agrees well with that obtained by other methods..

Furthermore
$$\frac{M'_{\text{H}}}{m} = \frac{e/m}{e/M'_{\text{H}}} = \frac{e/m}{f},$$

where f is the value of the Faraday. Vinal's[4] most recent work shows

[4] Vinal, Bur. Standards Sci. Papers, 218 and 271.

that this is not known with quite the precision ordinarily assumed, his extensive experiments giving $f = 96500 \pm 10$ coulombs. Accordingly

$$\left.\begin{aligned}\frac{e}{m} = f\frac{M'_{\mathrm{H}}}{m} = (96500)\ (1846.5) &= 1.7819\cdot 10^8 \text{ coulombs/g}\\ &= 1.7819\cdot 10^7 \text{ e.m.u./g}\\ &= 5.343\ \cdot 10^{17} \text{ e.s.u./g.}\end{aligned}\right\} \quad (12)$$

These values should be good to 1 part in 2000 so that the method affords one of the most precise means[5] for determining e/m.

Elliptical Orbits

The possibility of elliptical orbits for the revolving electron greatly complicates the problem by the introduction of a second degree of freedom, viz. variation in the length of the radius vector, but leads to results of the most fundamental nature.

In general, let us consider a system having k degrees of freedom. For the description of its configurations we require k independent coördinates, $q_1, q_2 \cdot \cdot \cdot q_k$. These may be, for example, the Cartesian or the polar coördinates of the various particles of the system. Corresponding to each q there will be a quantity p which plays the same mathematical rôle in the expression for the kinetic energy of the system as the components of momentum, $m\frac{dx}{dt}$, $m\frac{dy}{dt}$, $m\frac{dz}{dt}$ play in the formula for the kinetic energy of a single particle. Thus for a particle, in Cartesian coördinates, the kinetic energy,

$$T = \frac{m}{2}\left[\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right] = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right),$$

where p_x, p_y, and p_z are the components of momentum. It will be noted that if we write $\frac{dx}{dt} = v_x$, etc., then

$$\frac{\partial T}{\partial \dot{x}} = \frac{\partial T}{\partial v_x} = \frac{m}{2}\frac{\partial}{\partial v_x}\left(v_x^2 + v_y^2 + v_z^2\right) = mv_x = p_x,$$

and similarly for p_y and p_z.

[5] This statement is based on Paschen's estimate of the precision with which N_{H} and N_{He} may be empirically determined. Birge, Phys. R. 17, pp. 589–607 (1921), in a very thorough consideration of the measurements on the hydrogen lines, has concluded that $N_{\mathrm{H}} = 109677.7 \pm 0.2$. An uncertainty of ± 0.2 in N_{H} gives rise to a possible error of $\pm 0.5\%$ in $N_{\mathrm{He}} - N_{\mathrm{H}}$ of Equation (11), which is carried over directly in the final computation of e/m. A similar error in N_{He} would still further increase the uncertainty in the determination of e/m.

Likewise for any dynamical system we define the generalized moment p_i corresponding to the coördinate q_i to be

$$p_i = \frac{\partial T}{\partial \dot{q}_i}, \quad i = 1, 2 \cdots k.$$

Let us choose such generalized coördinates that the kinetic energy contains only the squares of the generalized moments p_i, so that no terms such as p_1p_2 occur. In general the square of each moment will be prefixed by a coefficient which may be a function of one or more of the coördinates q. For example, the expression for the kinetic energy of a particle of mass m in polar coördinates is

$$T = \frac{m}{2}\left[\left(\frac{dr}{dt}\right)^2 + r^2\left(\frac{d\phi}{dt}\right)^2\right] = \frac{1}{2m}\left[\left(m\frac{dr}{dt}\right)^2 + \frac{1}{r^2}\left(mr^2\frac{d\phi}{dt}\right)^2\right].$$

$m\frac{dr}{dt} = p_r =$ linear momentum in the direction of the radius vector;

$mr^2\frac{d\phi}{dt} = p_\phi =$ angular momentum about the origin.

Therefore $T = \frac{1}{2m}\left(p^2_r + \frac{1}{r^2}p^2_\phi\right)$.

Let the coördinates also be so chosen that the potential energy of the system consists of a sum of functions each of which depends upon one coördinate only. Thus the potential energy will have the form

$$E_p = f_1(q_1) + f_2(q_2) + \cdots f_k(q_k).$$

For all the systems with which we shall deal, such a choice of coördinates is possible.

The conditions by which we select discrete or quantized states of steady non-radiating motion for the dynamical system of the atom may be stated in terms of the above generalized coördinates as follows:

$$\left.\begin{aligned} &\int p_i dq_i = n_i h \\ \text{where} \quad &p_i = \frac{\partial T}{\partial \dot{q}_i}, \end{aligned}\right\} \qquad (13)$$

and where the integral is taken over a complete period of the coördinate in question. (We shall be concerned only with systems where each coördinate is periodic.) The k equations furnished by the above requirements are the quantizing conditions laid down independently by W. Wilson[6] and by Sommerfeld.[7]

[6] W. Wilson, Phil. Mag. 29, p. 795 (1915).
[7] Sommerfeld, "Atombau," any edition, preferably 3d.

As an example of the application of Equations (13) let us consider first the simple case, described earlier, of circular orbits. Here we have but one degree of freedom, the azimuth ϕ, since the radius vector is fixed in magnitude. The limits of integration are $\phi = 0$ and $\phi = 2\,\pi$, corresponding to one complete revolution of the electron. Thus:

$$T = \frac{1}{2}mv^2 = \frac{1}{2}mr^2\left(\frac{d\phi}{dt}\right)^2 = \frac{1}{2}mr^2\dot{\phi}^2$$

$$\therefore\ p_\phi = \frac{\partial T}{\partial \dot{q}} = \frac{\partial T}{\partial \dot{\phi}} = mr^2\dot{\phi}.$$

Hence $$\int p\,dq = \int_0^{2\pi} mr^2\dot{\phi}\,d\phi = 2\,\pi mr^2\dot{\phi} = n_a h$$

since $\dot{\phi}$ is constant. But $mr^2\dot{\phi}$ is the angular momentum of the electron. We have accordingly derived Equation (2) by the use of the more general relation (13).

The integer n_a in this case is known as the azimuthal quantum number since the integral to which it applies contains the azimuth as the independent variable.

In the case of elliptical motion the quantizing process must be applied in respect to both azimuth and radius as follows:

$$\text{azimuth:}\quad n_a h = \int p\,dq = \int_0^{2\pi} \frac{\partial T}{\partial \dot{\phi}}\,d\phi = 2\,\pi \times \text{angular momentum} \tag{14}$$

$$\text{radius:}\quad n_r h = \int p\,dq = \int_{\phi=0}^{2\pi} \frac{\partial T}{\partial \dot{r}}\,dr. \tag{15}$$

The integer n_r is known as the radial quantum number since the independent variable in Equation (15) is the radius r. If we substitute in this the value of the kinetic energy we obtain from (14) and (15)

$$1 - \epsilon^2 = \frac{n_a^2}{(n_a + n_r)^2}, \tag{16}$$

in which ϵ is the eccentricity of the elliptical orbit. Thus not only must the angular momentum of the electron have certain discrete values but at the same time the shapes of the elliptical orbits are restricted in a very definite manner.

If we now evaluate the total energy $W_{n_a n_r}$ of the electron in any particular orbit determined by the azimuthal quantum number n_a and the radial quantum number n_r, we find

$$W_{n_a n_r} = -\frac{Nhc}{(n_a + n_r)^2}. \tag{17}$$

It will be noted that several different orbits exist, depending upon how the total value of $n_a + n_r$ is obtained, for which the energy has the same value. For example the orbit $n_a = 1$, $n_r = 2$ has the same energy as the orbit $n_a = 2$, $n_r = 1$ since $n_a + n_r = 3$ in each case.

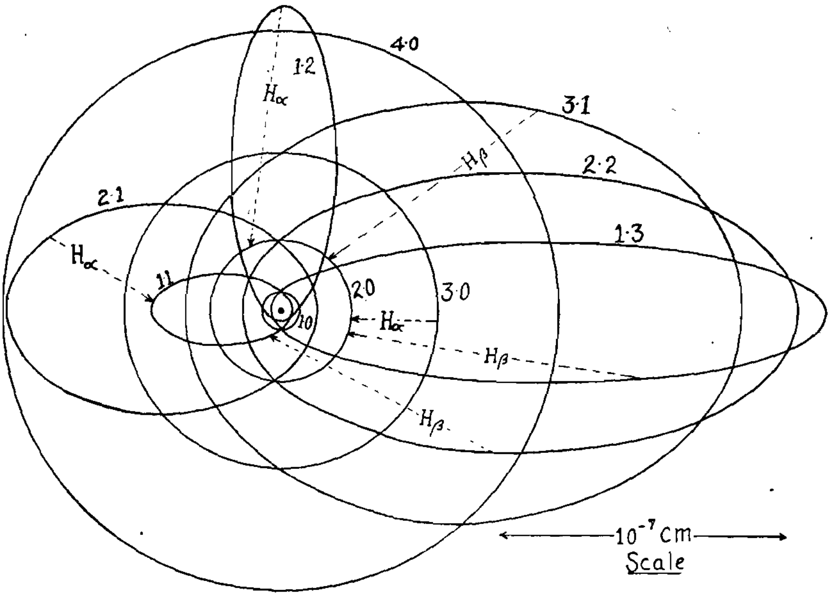


FIG. 1. A few of the inner orbits which may be occupied by the electron of the hydrogen atom. Actually these orbits are perturbed so that they are not exactly closed or cyclic. There is present a *slow* progressive motion of perihelion. The illustration represents very closely an "instantaneous photograph" of the possible states, while a "time exposure" would give a solid field of ink on account of the progressive motion.

Proceeding now in the same manner as that in which Equation (6) was derived and putting the difference in the total energies of two orbits $W_{n_a n_r}$ and $W_{n'_a n'_r}$ equal to h times the frequency of the emitted radiation, or hc times the wave number ν, we obtain the following spectral series formula:

$$\nu = N\left\{\frac{1}{(n'_a + n'_r)^2} - \frac{1}{(n_a + n_r)^2}\right\}. \qquad (18)$$

This again represents the series lines of hydrogen. The Balmer series is obtained when $n'_a + n'_r = 2$ and $n_a + n_r = 3, 4, 5$, etc. The physical significance of this more complicated formula will appear later.

It may be readily shown that all elliptical orbits, for which the total energy, W, of the atom is the same—cf. Equation (17)—have equal semi-major axes, a, and that the semi-minor axes, b, have the magnitudes:

$$b = \frac{n_a}{n_a + n_r} a. \tag{19}$$

All orbits for which $n_a = 0$ are straight lines through the nucleus and are hence excluded as physically impossible. We shall consider the form of the various inner orbits for the hydrogen atom, subject to the condition $n_a \neq 0$. The inmost orbit is obtained when $n_a + n_r = 1$, that is, when $n_a = 1$, $n_r = 0$. The next group of orbits is found by making $n_a + n_r = 2$. Proceeding in this manner we may by the help of Equation (19) compute the constants of the orbits, as given in Table I, and further illustrated by Figure 1.

TABLE I

ORBITS OF HYDROGEN TO $n_a + n_r = 4$

$n_a + n_r$	n_a	n_r	a	b	Form of Orbit
1	1	0	a_1	a_1	circle
2	2	0	$4a_1$	$4a_1$	circle
2	1	1	$4a_1$	$2a_1$	ellipse
3	3	0	$9a_1$	$9a_1$	circle
3	2	1	$9a_1$	$6a_1$	ellipse
3	1	2	$9a_1$	$3a_1$	ellipse
4	4	0	$16a_1$	$16a_1$	circle
4	3	1	$16a_1$	$12a_1$	ellipse
4	2	2	$16a_1$	$8a_1$	ellipse
4	1	3	$16a_1$	$4a_1$	ellipse

The line H_α is produced by an electron jumping from an orbit $n_a + n_r = 3$ to an orbit $n_a + n_r = 2$. Since there are three orbits of equal energy value for which $n_a + n_r = 3$ and two orbits for which $n_a + n_r = 2$, the line H_α may be produced in six different ways. Similarly H_β and H_γ may be produced in eight and ten different ways respectively. These

conclusions, however, must be considerably modified, as will appear directly.[8]

Relativity of Mass

The first modification, due to Sommerfeld[9], arises in the fact that the mass of the electron in its elliptical orbit is not a constant but depends upon its velocity, v, thus: $m = m_0 \sqrt{1 - \beta^2}$, where $\beta = v/c$ and m_0 is the mass of a stationary or slow-moving electron. From a mathematical standpoint the character of the orbit is considerably changed thereby, but if the velocity of the electron is moderate compared to that of light, we may consider the path as an ellipse with slowly moving perihelion. Corresponding to Equation (17) we now obtain Equation (20) for the energy of the electron in the $n_a n_r$ orbit.

$$W_{n_a n_r} = -\frac{NhcZ^2}{(n_a + n_r)^2}\left[1 + \frac{\alpha^2 Z^2}{(n_a + n_r)^2}\left(\frac{1}{4} + \frac{n_r}{n_a}\right) + \cdots\right], \tag{20}$$

where $$\alpha = \frac{2\,\pi e^2}{hc}. \tag{21}$$

In this relation α^2 is a relatively small quantity being equal to $5.31 \cdot 10^{-5}$; hence it is sufficient for the present to neglect terms of higher order

[8] It is of interest to note that there exists a perfectly general relation between the frequency of revolution of the electron about the nucleus and the wave number or the frequency of the radiation emitted when the electron falls from one orbit to another.

It may be readily shown that the frequency of revolution, f, of the electron moving in an elliptical orbit about the positive charge E is given by the relation

$$f = \frac{eE}{ah\,(n_a + n_r)} \quad \text{where} \quad a = \frac{h^2}{4\,\pi^2 meE}(n_a + n_r)^2.$$

On replacing a in the first equation by its equivalent, we obtain

$$f = \frac{4\,\pi^2 me^2E^2}{h^3(n_a + n_r)^3} = \frac{2\frac{E^2}{e^2}Nc}{(n_a + n_r)^3} \qquad \text{(by Equation 7)}$$

or, for hydrogen, $$f = \frac{2\,Nc}{(n_a + n_r)^3} \qquad \text{for the initial orbit}$$

and $$f' = \frac{2\,Nc}{(n'_a + n'_r)^3} \qquad \text{for the final orbit.}$$

Replacing the terms $(n_a + n_r)^2$ and $(n'_a + n'_r)^2$ of Equation (18) by the values from the above relations we find directly

$$\nu = \frac{1}{2\,c}\left\{(n'_a + n'_r)f' - (n_a + n_r)f\right\}.$$

If this is expressed in terms of the total quantum number $n = n_a + n_r$ and frequency ν ($= c\nu$) instead of ν, we obtain

$$\bar{\nu} = \frac{1}{2}\left(n'f' - nf\right).$$

Hence the frequency of the emitted radiation is one-half the difference of the products of the total quantum number and the frequency of revolution of the electron in each of the orbits concerned in the transfer. This is a general law immediately applicable to any spectrum of the hydrogen type, such as that of ionized helium, doubly ionized lithium, etc. If $n - n' = 1$ where both n and n' are large $\bar{\nu} \sim f$, that is, the frequency of the emitted light is approximately equal to the frequency of revolution of the electron in its orbit. This approximation of the quantum theory to the classical dynamics for small frequencies or long wave-lengths has an analogy in the law of the spectral distribution for black-body emission, where the Planck relation approximates the classical Rayleigh equation for long wave-lengths.

[9] See general reference 3 at end of chapter.

...LLEGE AN... ...TITUTE

than α^2. The first term of this general equation is identical with Equation (17) (for hydrogen, $Z = 1$). The second and succeeding terms are the corrections introduced by the relativity considerations. We note that whereas in Equation (17) n_a and n_r occurred together as a sum, in the correction term of Equation (20) they also occur as a quotient. The energies of the various "elliptical" orbits in Figure 1, for the same total quantum number accordingly depend upon how this number is obtained. For example the energy is slightly different for the orbits characterized by $n_a + n_r = 1 + 2 = 3$; $n_a + n_r = 2 + 1 = 3$ and $n_a + n_r = 3 + 0 = 3$. Thus the six possible transfers from $n_a + n_r = 3$ to $n_a + n_r = 2$ will produce six slightly different frequencies. These frequencies or wave numbers may be computed from Equation (22) which is analogous to Equation (18) derived without relativity considerations.

$$\nu = NZ^2\left[\frac{1}{(n'_a + n'_r)^2} + \frac{\alpha^2Z^2}{(n'_a + n'_r)^4}\left(\frac{1}{4} + \frac{n'_r}{n'_a}\right) - \frac{1}{(n_a + n_r)^2} - \frac{\alpha^2Z^2}{(n_a + n_r)^4}\left(\frac{1}{4} + \frac{n_r}{n_a}\right)\right]. \tag{22}$$

Hence the line H_α which represents an interorbital transfer from total quantum numbers 3 to 2, when resolved by a high power spectroscope such as an echelon grating, should show fine structure and should appear as a group of fine lines. The six mathematically possible components for H_α, computed by Equation (22), where for N is substituted N_H thus taking into account the finite mass of the nucleus, are given in Table II.

TABLE II

FINE STRUCTURE OF H_α

ν	λ Vacuum	$n_a n_r \rightarrow n'_a n'_r$	Δn_a	Remarks See page 26
15233.451	6564.501	30 → 11	− 2	excluded
3.415	.516	21 → 11	− 1	
3.307	.563	12 → 11	0	excluded
3.086	.658	30 → 20	− 1	
3.050	.674	21 → 20	0	excluded
2.941	.720	12 → 20	+ 1	

In the same manner the fine structure of other Balmer lines and lines of the Lyman and Paschen series may be computed. With $Z = 2$ in

Equation (22) we may similarly predict the fine structure of the series lines of ionized helium.

The Principle of Selection

The second modification of the simple theory consists in the application of the principle of selection. So far in the analysis we have utilized the principle of the conservation of energy as applying to the coupled action between the ether and matter. The energy lost by the atom when the electron is transferred from an orbit of higher energy level to one of lesser energy is conserved by the ether in the form of radiation of frequency $\bar{\nu}$ or wave number ν given by Equation (22). Keeping the original Bohr postulates which included the principle of conservation of energy we shall now additionally restrict the problem by the condition that we have conservation of moment of momentum.[10] That is, the moment of momentum lost by the mechanical system forming the atom, in any interorbital transition, is conserved by the ether as moment of momentum of radiation. By a simple mathematical analysis Rubinowicz[11] showed that these assumptions lead to the conclusions that in any interorbital transition of an electron, resulting in radiation, and not complicated by the presence of an electrostatic or magnetic field, the azimuthal quantum number n_a may change by -1, 0 or $+1$ and by no other amount. Bohr[12] has derived a more restricted principle of selection which excludes the zero change of momentum. For the present we shall confine our discussion to the Bohr restricted principle which may be stated as follows:

$$\Delta n_a = n'_a - n_a = +1 \text{ or } -1. \qquad (23)$$

Applying this principle to the analysis of the fine structure of H_α, of the six mathematically possible transitions three are excluded as shown in the last two columns of Table II, because for these the change in azimuthal quantum number is not ± 1. Hence we arrive at the final conclusion that the line H_α is made up of three components. On account of the difference in energy of the two *final* orbits, $n_a + n_r = 1 + 1$ and $n_a + n_r = 2 + 0$, these three lines may be considered as a doublet one component of which has a satellite. Similarly with H_β for which, of the $4 \times 2 = 8$ mathematically possible transitions, all but three are excluded by the selection principle. The interorbital transitions resulting in H_α and H_β are shown by dotted lines in Figure 1.

[10] For a concise statement of the conceptions here involved, see Sommerfeld, "Atombau," 3d Ed., pp. 310–39.

[11] Rubinowicz, Physik. Z. 19, pp. 441, 465 (1918).

[12] See general reference 2. Also Dushman, J. Opt. Soc. Am. & R. S. I., 6, p. 235 (1922).

Experimental Verification by Fine Structure Analysis

The experimental verification of the above deductions in the case of the hydrogen atom is probably as satisfactory as could be expected at the present time. Referring to Table II it is seen that the entire fine structure of H_α should cover a spectral range of only 0.2 A. Now the width[13] of a spectral line, assuming it may be accounted for by the Doppler-Fizeau effect, may be shown[14] to be

$$\Delta \doteq 0.86 \cdot 10^{-6} \lambda \sqrt{T/M},$$

where T is the absolute temperature and M the molecular weight of the radiating gas.

Since $M = 1$ for the hydrogen atom it is readily apparent that the precision of measurement of fine structure will be seriously affected by the Doppler effect. Even with the discharge tube immersed in liquid air the theoretical width of each component of H_α is 0.051 A. However, the component of longest wave-length should be weak, and it may be shown that the separation of this component and the central component should be only about 4/10 the separation of the central component and the one of shortest wave-length. This results in the obervation of the triplet as a *doublet* with fairly wide components arising from the Doppler effect. The observed separation of this doublet is obviously not the theoretical doublet separation shown by the braces in the first column of Table II, which has the computed magnitude $\Delta\nu_H = 0.365$ cm^{-1}. It is possible to compute from the theoretical distribution of the lines what magnitude of the doublet separation should be observed. Or conversely, the observed separations when corrected should afford a check upon the theoretical deductions. We have, however, in addition to the distribution of intensity produced by the Doppler effect, in any laboratory experiment, broadenings of each component arising in the Stark effect, imperfect focus upon the plate, spreading of the image on the emulsion, and mechanical difficulties. These effects combine in producing an apparent narrowing of the observed doublet. The following table summarizes the data on H_α by several observers where we are not certain of the methods employed in determining these various correction factors. In fact, some of these corrections have not been applied to the first three values given.

[13] Measured at the point where the intensity has decreased to $1/e$ of its maximum value.
[14] The method of derivation of this and similar formulae is summarized by Nagaoka, Proc. Math. Phys. Soc. Tokyo, 8, pp. 237–43 (1915).

$\Delta\nu_H$	Observer	Reference
.34 cm^{-1}	Merton	Proc. Roy. Soc. 97, p. 307 (1920)
.29	Gehrcke and Lau	Physik. Z. 21, p. 634 (1920)
.36	McLennan and Lowe	Proc. Roy. Soc. 100, p. 217 (1921)
.35	Oldenberg	Ann. Physik, 67, p. 453 (1922)

It is seen that the agreement between the observed and compute values is fairly satisfactory. However, when the measurements ar extended to other lines in the Balmer series there appears to be a sligh systematic decrease in the doublet separation, measured in cm^{-1}, as on proceeds to the higher terms of the series. It is doubtful whether th above-mentioned disturbing effects are adequate to account complete for existing observations on H_β, H_γ, and H_δ. Ruark has suggested t the authors that there still remain to be considered disturbances arisin in (1) finite size of nucleus[15] and (2) possible magnetic moment o nucleus. Any correction arising from a consideration of retarded po tentials has been shown by Darwin[16] to be less than 0.001 A and t affect all components of a given line in the same manner.

The real experimental verification of the theory lies in Paschen' analysis of certain lines of ionized helium.[17] Since for helium M = the Doppler effect is considerably decreased, and since $Z = 2$ we hav a more open scale of ν, as is apparent from Equation (22). The heliun line λ 4686 is produced by a transfer of the remaining electron in th ionized atom from orbits of total quantum number 4 to orbits of tota quantum number 3. Twelve lines are thus mathematically possible but the application of the Bohr principle of selection reduces this numbe to five. Figure 2, adapted from Sommerfeld's "Atombau," 2d ed., p 350, shows, below, the wave-lengths observed by Paschen, the height of the shaded portions representing intensity. Above the observe wave-lengths are those computed by means of Equation (22), using th selection principle. At the top, shown by dotted lines, are the mathematically possible lines computed directly from Equation (22). Th entire wave-length scale covers an interval of only 0.8 A. or about of the distance between the two D-lines of sodium, and yet the theoretically predicted fine structure is well confirmed by the experimental

[15] Silberstein, Phil. Mag. 39, p. 46 (1920), has given the method of computing corrections for an aspherical nucleus.
[16] Phil. Mag. 39, p. 537 (1920).
[17] Paschen, Ann. Physik, 50, pp. 901–40 (1916).

data. The two lines marked *d*, while mathematically possible, involve a change in the azimuthal quantum number of two units and hence by the principle of selection should not exist. However, this principle was established conditionally upon the absence of an electrostatic or electromagnetic field. On the other hand such a field is present in a high voltage discharge tube. A thorough consideration of the phenomena in the presence of disturbing fields requires the application of the quantum theory to the Stark and Zeeman effects,[18] quite beyond the scope of the present work. Suffice to say that as a result of such analysis it may be shown that the lines marked *d* should appear in a weak electrostatic field, and still other lines should be excited with higher potentials, in agreement with further observations of Paschen.[19]

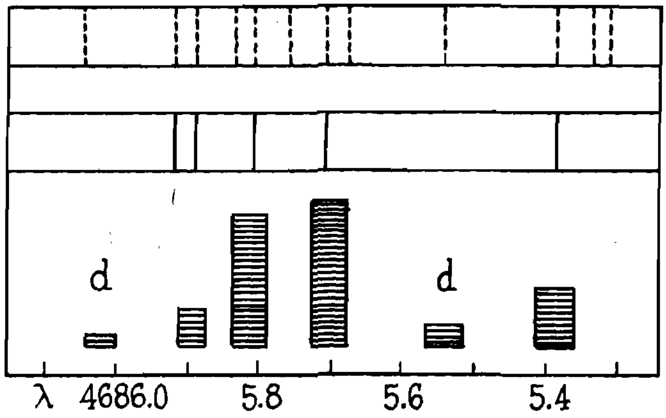


Fig. 2. Fine structure of the helium line λ 4686.

In the case of H_α we have seen that the fine structure consists of fundamental doublet with a satellite. The doublet separation $\Delta\nu$ is due to the difference in energy of the two final orbits $1 + 1 = 2$ an $2 + 0 = 2$. This value of $\Delta\nu_H$ is readily obtained from Equation (22 by putting $\Delta\nu = \nu_1 - \nu_2$, where ν_1 refers to $n'_a = 1$, $n'_r = 1$ and an value of n_a and n_r and where ν_2 refers to $n'_a = 2$, $n'_r = 0$ with the sam values of n_a and n_r. Hence since $Z = 1$ for hydrogen, we obtain

$$\Delta\nu_H = \frac{N\alpha^2}{16} = 0.365\ \mathrm{cm}^{-1}. \qquad (24$$

[18] Kramers, Copenhagen Acad., 1919. See also general references 2, 3, 4, 6, 7, at end chapter.
[19] Paschen, loc. cit.

Now Equation (22) may be rewritten with $N\alpha^2$ replaced by 16 $\Delta\nu_H$ and the new formula used for estimating the separation of the components of the helium lines in terms of $\Delta\nu_H$. Or conversely, these separations may be determined experimentally for helium and used to compute the value of $\Delta\nu_H$ for hydrogen. In this latter manner Paschen found experimentally

$$\Delta\nu_H = 0.3645 \pm 0.0045 \text{ cm}^{-1},$$

in agreement with the theoretical value of $\Delta\nu_H$ given by Equation (24).

Atoms with Many Electrons

Evidence from various sources, both physical and chemical, enables us to derive some information in regard to the distribution of electrons about the nucleus. The periodic table of chemical elements furnishes an important clue as to the electron arrangement. The present viewpoint is that the intervals between rare gases, and not the rows of the table, give the true periods of the atomic systems.

The chemical inactivity of the rare gases suggests that these elements represent completed structures. With the intermediate elements only superficial changes in the electron configuration occur. At each new period a "shell" is added to the original structure. An atom is characterized by as many groups or "shells" of electrons as the numerical value of the period which it occupies, viz., He one, A three, etc. The number of electrons in each group when completed has been considered equal to the number of elements in the corresponding period. That is, in successive groups from the center out, the number of electrons, on this hypothesis, follows the distribution law 2, 8, 8, 18, 18, 32.

The *new* Bohr[20] theory of atomic structure retains the above conception of groups of electrons corresponding to periods in the chemical properties but postulates the occurrence of changes in *inner* groups as well as in the *outer* shell. The resulting distribution for several families is given in Table III, in which K, L, M, etc., follow the usual x-ray notation for successive layers.

As to the orientation of these electrons, many different theories have been proposed. The Lewis-Langmuir[21] hypothesis postulates for each group a cubical distribution of electrons in which motions are limited to relatively small vibrations about positions of equilibrium. Such a model is not easily reconciled with the viewpoint of the spectroscopist.

[20] Bohr, Z. Physik, 9, pp. 1–67 (1922).
[21] Langmuir, J. Am. Chem. Soc., 38, p. 762 (1916); 41, p. 868 (1919).

TABLE III

GROUPING OF ELECTRONS IN ATOMS

Element	Z	K	L	M	N	O	P	Q
He	2	2						
Ne	10	2	8					
A	18	2	8	8				
Kr	36	2	8	18	8			
Xe	54	2	8	18	18	8		
Nt	86	2	8	18	32	18	8	
Li	3	2	1					
Na	11	2	8	1				
K	19	2	8	8	1			
Cu	29	2	8	18	1			
Rb	37	2	8	18	8	1		
Ag	47	2	8	18	18	1		
Cs	55	2	8	18	18	8	1	
Au	79	2	8	18	32	18	1	
Be	4	2	2					
Mg	12	2	8	2				
Ca	20	2	8	8	2			
Zn	30	2	8	18	2			
Sr	38	2	8	18	8	2		
Cd	48	2	8	18	18	2		
Ba	56	2	8	18	18	8	2	
Hg	80	2	8	18	32	18	2	
Ra	88	2	8	18	32	18	8	2

The configuration originally proposed by Bohr[22] and generally adopted in the past for the extension of the Bohr theory to atoms with many electrons, consisted of coplanar, concentric rings of electrons revolving about the nucleus. The possibility of elliptical orbits complicates the problem, for while several electrons may be stable in the same circular orbit only one electron may occupy an elliptical orbit. However, it is readily possible to so orient a group of similar, coplanar, confocal ellipses, each containing one electron, that at every instant all the electrons of any one group lie on a circle concentric with the nucleus.

The recently proposed theory of Bohr (see Appendix II) on which the distribution of electrons in Table III is based, denies the possibility of the formation of a ring model, in spite of its mechanical stability,

[22] See general reference 1 at end of chapter.

and assumes that each electron moves in an individual orbit and in general in an individual plane. The resulting space configuration through which the chemical properties of the elements may be interpreted leads to insurmountable difficulties in the mathematical analysis of the motion of the electrons in heavy atoms, except for qualitative deductions.

Accordingly, while recognizing that the electrons are actually revolving in elliptical orbits in different planes, orbits such that those of greater quantum number and eccentricity may penetrate nearer to the nucleus than those of lesser quantum number but more nearly circular, we shall for the simplification of the mathematical treatment adopt the Sommerfeld[23] conceptions.

That the postulating of a ring configuration for the inner electrons frequently is an approximation to fact which is justified as far as the motion of an outer electron is concerned will be evidenced by the striking experimental verification of the conclusions drawn in the following sections.

Derivation of the Ritz Equation

The Ritz equation represents the variable term in a spectral series formula for elements containing several electrons. The original derivation of this relation was purely empirical, but Sommerfeld[24] has recently shown that it possesses some physical significance. We note from Table III that the alkalis have one outer electron. As an approximation Sommerfeld assumed that all the other electrons could be considered to be in a single circular orbit. In general then we assume a core of positive charge Ze surrounded by a circular ring of radius a_0 containing $p = Z - k$ electrons, in turn surrounded by the coplanar, and in general elliptical, orbits of the *single* remaining electron. The outer electron is responsible for the emission of the ordinary spectral lines. Such an atom resembles the simple structure for hydrogen except that the outer electron is no longer in a Coulomb field, on account of the disturbing action of the ring of electrons. In assuming elliptical orbits we introduce two degrees of freedom, requiring as in the general case for hydrogen, the application twice of the quantizing integral $\int pdq = nh$. The ring of electrons may be considered as a ring of uniform distribution of charge of total value $-(Z - k)e$, and of radius a_0. We desire the total energy $W_{n_a n_r}$ of the electron in the orbit having as azimuthal and

[23] "Atombau."
[24] "Atombau," 2d ed., Appendix 13.

radial quantum numbers the integers n_a and n_r respectively and radius vector of length r. This is equal to the sum of the potential energy E_P and the kinetic energy T for the same orbit. We find:

$$E_P = -\frac{k\epsilon^2}{r} + \frac{c_1}{r^3} + \frac{c_2}{r^5} + \cdots, \tag{25}$$

where $$c_1 = \frac{1}{4}\left(Z - k\right) e^2 a_0^2 \text{ and } c_2 = \frac{9}{64}\left(Z - k\right) e^2 a_0^4, \tag{26}$$

$$T = \frac{1}{2m}\left(p^2_r + \frac{1}{r^2} p^2_\phi\right). \tag{27}$$

Applying the first quantizing integral:

$$\int_0^{2\pi} p_\phi d\phi = 2\pi p_\phi = n_a h. \tag{28}$$

Substituting this value of p_ϕ in (27), adding (27) and (25), equating to the total energy W, and solving for p_r we obtain for the second quantizing process:

$$\int p_r dr = \int \sqrt{2mW + \frac{2mke^2}{r} - \frac{1}{r^2}\frac{n^2h^2}{4\pi^2} - \frac{2mc_1}{r^3} - \frac{2mc_2}{r^5}}\, dr = n_r h. \tag{29}$$

This complicated integral, evaluated over a complete period, gives:

$$W_{n_a n_r} = -\frac{Nhck^2}{\left(n_a + n_r + a - \alpha\frac{W}{h}\right)^2}. \tag{30}$$

The constants a and α in this equation are complicated, but to terms of the first order are as follows:

$$a = \frac{(2\pi)^4 m^2 ke^2 c_1}{n_a^3 h^4}, \tag{31}$$

$$\alpha = -3\frac{(2\pi)^6 m^3 ke^2 c_2}{n_a^5 h^5}. \tag{32}$$

Putting, as heretofore, the difference in total energies of two orbits $W_{n_a n_r}$ and $W_{n'_a n'_r}$ equal to hc times the wave number of the emitted radiation we obtain the following spectral series formula.

$$\nu = k^2 N\left[\frac{1}{[n'_a + n'_r + a' - \alpha' c(m', a')]^2} - \frac{1}{[n_a + n_r + a - \alpha c(m, a)]^2}\right]. \tag{33}$$

$$m = n_a + n_r, \qquad (m, a) = W - /hc.$$

This is the familiar Ritz equation, originally derived empirically.

Application of the Ritz Equation

There are four important series in the arc spectra of the alkalis known as the Principal, 1st Subordinate, 2d Subordinate and Bergmann Series. Developed empirically these series are represented as follows. where s, σ, p, π, d, δ, b and β are constants.

Principal:

$$\nu = \frac{N}{[m' + s + \sigma(m', s)]^2} - \frac{N}{[m + p + \pi(m, p)]^2}. \tag{34}$$

$$m' = 1, \quad m = 2, 3, 4, \text{ etc.}$$

1st Subordinate:

$$\nu = \frac{N}{[m' + p + \pi(m', p)]^2} - \frac{N}{[m + d + \delta(m, d)]^2}. \tag{35}$$

$$m' = 2, \quad m = 3, 4, 5, \text{ etc.}$$

2d Subordinate:

$$\nu = \frac{N}{[m' + p + \pi(m', p)]^2} - \frac{N}{[m + s + \sigma(m, s)]^2}. \tag{36}$$

$$m' = 2, \quad m = 2, 3, 4, \text{ etc.}$$

Bergmann:

$$\nu = \frac{N}{[m' + d + \delta(m', d)]^2} - \frac{N}{[m + b + \beta(m, b)]^2}. \tag{37}$$

$$m' = 3 \quad m = 4, 5, 6, \text{ etc.}$$

The first term in each of the above formulae has a fixed value of m' and is accordingly constant. In shorthand notation these series relations may be written:

Principal	$\nu = 1\,s - mp,$	$m = 2, 3, 4$	(38)
1st Subordinate	$\nu = 2\,p - md,$	$m = 3, 4, 5$	(39)
2d Subordinate	$\nu = 2\,p - ms,$	$m = 2, 3, 4$	(40)
Bergmann	$\nu = 3\,d - mb,$	$m = 4, 5, 6$	(41)

On comparing Equations (34) to (37) with Equation (33) we identify a successively with the constants s, p, d and b and $-\alpha c$ with the constants σ, π, δ and β. By definition of k we have $k = 1$ for the alkalis. Referring to Equation (31) we note that a is proportional to $1/n_a^3$, *i.e.* a function of the azimuthal but not of the radial quantum number. Hence in order that $a = s$ be a constant for all the ms terms, such terms must be characterized by a *constant* azimuthal quantum number, the variation in $m = n_a + n_r$ being due to the radial quantum number alone.

Similar conclusions are necessary for the *mp*, *md* and *mb* terms. These conclusions are again substantiated by the fact that α in Equation (32) likewise is a function of n_a but not of the variable n_r.

Equation (34) shows that the lowest value[25] of m for the *ms* terms is 1. Since $m = 1 = n_a + n_r$, and since $n_a \neq 0$ because this gives the impossible rectilinear vibration through the nucleus, we conclude that $n_a = 1$ for all *ms* terms. *All* the *ms* terms are therefore characterized by an azimuthal quantum number 1 and by a radial quantum number from 0 to ∞. The principal series involves combinations of *ms* and *mp* terms. By the Bohr principle of selection the azimuthal quantum number n_a may change by only + 1 or − 1. Hence in the transition from the *mp* orbit to the *ms* orbit, since n_a cannot be zero, the electron must go from an orbit where $n_a = 2$ to an orbit where $n_a = 1$. *All mp* orbits are therefore characterized by an azimuthal quantum number 2 and by a radial quantum number from 0 to ∞.

We see accordingly a common property in that the radial quantum numbers for both terms may assume *any* positive integral value including zero, the latter value referring to a circular orbit. The minimum value of m for the *md* terms is 3 and for the *mb* terms 4. Hence if these terms likewise refer to circular orbits, that is if n_r can become zero, we may conclude that all *md* terms are associated with the constant azimuthal quantum number 3 and the *mb* terms with the azimuthal number 4. These conclusions are summarized in Table IV.

TABLE IV

AZIMUTHAL AND RADIAL QUANTUM NUMBERS

Variable Term	Quantum Number	
	Azimuthal	Radial
ms	1	0 to ∞
mp	2	0 to ∞
md	3	0 to ∞
mb	4	0 to ∞

It is now seen why series of the type given by Equations (38) to (41) should predominate and not other combinations. The old Ritz principle of combination stated that any pair of series terms could be used in

[25] Obviously in discussing *numerical* values of series terms, the symbols m and m', which respectively distinguish initial and final states, are interchangeable: thus $2s = 2's$.

combination to give a spectral line. We now associate a definite azimuthal quantum number with each of the s, p, d and b terms and by the Bohr principle of selection only such combinations may occur for which $n_a = -1$ or $+1$. Hence we should not expect lines such as $\nu = m's - mb$ since these involve a change of three units in the azimuthal quantum number. The change in azimuthal quantum number for each of the four series, Equations (38) to (41), is $\Delta n_a = \pm 1$. Since the minimum value of $n_a + n_r$ occurs when $n_r = 0$, we see why these four series begin with peculiar, fixed values of m, the minimum or initial value being determined by the azimuthal quantum number associated with the variable term (except for the 2d subordinate series where $m_{min} = n_a + n_r = 1 + 1$).

Exceptions to these deductions may be found. A similar exception has been noted with helium where certain components for which $\Delta n_a = 2$ appear in a high voltage discharge. Thus with the alkalis we find lines such as $\nu = 2p - mp$, $1s - ms$, $3d - md$ for which the change in azimuthal quantum number is zero. This fact, however, would not be contradictory to the less restricted Rubinowicz principle of selection. A more serious exception occurs in such lines as $\nu = 1s - md$ where the change in azimuthal quantum number is two units. All of these exceptions have been, as with helium, attributed to the disturbing effect of the electrostatic exciting field, under which condition their presence is in accord with the theory. Foote, Mohler and Meggers,[26] on the other hand observed $1s - 3d$ for sodium and potassium in a discharge tube completely shielded from any applied field. The above conclusions are, however, in general well confirmed, and even though the theory is not completely satisfactory, still it contains much of great value and interest.[27]

Since we are concerned in this book only with the more important general principles we are not able to extend the theory to doublet and triplet spectra,[28] which at present is in a less satisfactory state of development. The spectra of the alkalis are characterized by close doublets, as for example the two D-lines of sodium. The mp terms are associated with double p orbits p_1 and p_2 of slight energy difference. Hence the lines of the principal series are designated by $1s - mp_1$ and $1s - mp_2$. Similarly with the metals of the second group of the periodic table which are characterized by rather widely separated triplets arising in the

[26] Phil. Mag., 43, pp. 659–61 (1922).

[27] Probably all of these exceptions can be explained by the electrostatic field arising in neighboring atoms and ions.

[28] Sommerfeld, "Atombau," 3d ed., Chap. 6, Section 5.

threefold p orbits, p_1, p_2 and p_3. The latter family also has many single lines grouped in series. Single lines are designated in the same notation except that capital letters are used, as for example $1\ S - mP$, which represents important fundamental lines. We also find for these elements combination series, one term belonging to the single line group and the other to a triplet group, as for example $1\ S - mp_2$, another fundamentally important series.

Fine Structure, Doublets and Triplets

It must be emphasized that the fine structure of hydrogen and of ionized helium has nothing in common with the fine structure, doublets, triplets, satellites, etc., of the more complex elements. It appears rather that the disturbing action of the inner groups of electrons in the complex atoms opens out into several series what would otherwise have been true fine structure. Or put conversely, the components in the fine structure of the Balmer lines of hydrogen are really terms of its principal and subordinate series, which, because of the strictly Coulomb field, are not widely separated. Thus on considering the interorbital transitions involved we may by analogy with the alkalis orient the Balmer lines as shown in Table V.

TABLE V

Fine Structure of Balmer Lines

Line	$n'_a + n'_r \leftarrow n_a + n_r$	Series Notation	
H_α	$2 + 0 \leftarrow 3 + 0$	$2\ p - 3\ d$	1st Sub.
	$2 + 0 \leftarrow 1 + 2$	$2\ p - 3\ s$	2d Sub.
	$1 + 1 \leftarrow 2 + 1$	$2\ s - 3\ p$	Prin.
H_β	$2 + 0 \leftarrow 3 + 1$	$2\ p - 4\ d$	1st Sub.
	$2 + 0 \leftarrow 1 + 3$	$2\ p - 4\ s$	2d Sub.
	$1 + 1 \leftarrow 2 + 2$	$2\ s - 4\ p$	Prin.
etc.			

Nuclear Defect of a Ring of Electrons

In succeeding discussions it is necessary to consider the shielding action on the nucleus by a ring of several electrons. From purely geometrical considerations, assuming the inverse square law, it may be shown that the force, which is radial, acting on any one of n electrons,

symmetrically distributed in a ring, of radius a_0, with the charge $+ Ze$ at the center, is:

$$\text{Force} = \frac{Ze^2}{a_0^2} - \frac{e^2}{4\,a_0^2}\sum_{k=1}^{k=n-1} cosec\,\frac{\pi k}{n} \tag{42}$$

$$= \frac{e^2}{a_0^2}(Z - s_n), \tag{43}$$

where $$s_n = \frac{1}{4}\sum_{k=1}^{k=n-1} cosec\,\frac{\pi k}{n}. \tag{44}$$

The quantity s_n is called the nuclear defect of the ring of n electrons and $Z' = Z - s_n$ the "effective" core charge. For large values of n, above 10 to 20, we may represent s_n approximately by the simple formula:

$$s_n = \frac{n}{2\,\pi}(nat\,ln\,n + 0.12). \tag{45}$$

The radius of a single ring of n electrons about a nuclear charge Ze is as follows:

$$a_0 = \frac{a_h}{Z - s_n} = \frac{a_h}{Z'}, \tag{46}$$

where a_h is the radius of the hydrogen atom. **From** Equations (1) and (3) we find for an azimuthal quantum number **1**:

$$a_h = \frac{h^2}{4\,\pi^2 me^2}. \tag{47}$$

In case the electrons are distributed in two concentric rings, in ccordance with our interpretation of the quantum theory, we assign o each electron in the inner ring one unit of angular momentum and to ach electron in the outer ring two units. Hence for a ring of radius a_1 containing p electrons and an outer ring of radius a_2 containing q electrons we find:

$$a_1 = \frac{1^2\,a_h}{Z - s_p}, \tag{48}$$

$$a_2 = \frac{2^2\,a_h}{Z - p - s_q}. \tag{49}$$

The total **energy** of the p electrons in the inner ring and that of the q electrons in **the** second ring may be shown to have the values:

$$W_p = -\,p\,\frac{Nhc}{1^2}(Z - s_p)^2, \tag{50}$$

$$W_q = -q\frac{Nhc}{2^2}(Z-p-s_q)^2. \tag{51}$$

It should be noted in Equations (49) and (51) that the inner ring is considered to be sufficiently close to the nucleus so that, as far as the outer ring is concerned, its nuclear defect is p, these p electrons simply decreasing the core charge by their total value pe. Similarly in Equations (48) and (50) the effect of the outer ring is neglected. It is accordingly evident that in considering the orbits of a single electron revolving outside of other rings of electrons, the number of electrons in the outer ring is a predominant factor, the exact distribution in the inner rings being of minor importance.

Spark Spectra

Spectral lines which arise in ionized atoms are called enhanced or spark spectra. Formerly they could be produced in the laboratory only by high voltage condenser discharge — whence the terminology "spark" spectra. We have already considered the enhanced spectrum of ionized helium and shall now discuss the spectra of the ionized alkali earths. Referring to Table III, we note that the normal atoms in this group all contain two electrons in the outer ring. We shall assume that one of these has been removed by the process of ionization. The structure then becomes identical with that of the alkali of next lower atomic number except that the core charge is one unit greater. This is equivalent to putting $k^2 = 4$ in Equation (33). The enhanced spectrum of ionized magnesium, accordingly, should resemble the arc spectrum of sodium, and similarly for the other pairs of elements in these two groups. The variable series term for these enhanced lines should by Equation (33) take the form:

$$(m, a^*) = \frac{4N}{[n_a + n_r + a^* - \alpha^* c\,(m, a^*)]^2}. \tag{52}$$

We note that since $k = 2$, the factor k^2N ($= 4\,N = A$) appears in the variable term of the enhanced spectra instead of simply N. This fact is fairly well substantiated by empirical computation[29] as shown in Table VI.

[29] Since this was written, Fowler's book on "Series in Line Spectra" has appeared. He has recomputed these series, using $A = 4N$ as predicted by theory. Table VI is accordingly of historical interest only. See section on "Spectroscopic Tables."

TABLE VI

CONSTANT IN ENHANCED SERIES FORMULAE

Element	Series	Constant = A	A/N
Mg..........	1st Sub.	423377	3.9
	2d Sub.	413202	3.8
Sr...........	1st Sub.	410836	3.7
	2d Sub.	415157	3.8
Ca...........	1st Sub.	423416	3.9
	2d Sub.	421559	3.8
Ba...........	1st Sub.	390431	3.6
	2d Sub.	397795	3.6

We shall now discuss the relation between the constants a^* for enhanced spectra of the alkali earths and the constants a for the arc spectra of the alkalis. In order to approximate physical conditions more closely, as shown by Table III, we shall consider two rings of electrons about the core, besides the orbit of the valence electron, the outer ring of radius a_2 containing, according to Table III, $q = 8$ electrons and the inner ring of radius a_1 containing $p = Z - q - k$ electrons. The remaining valence electron revolves about this entire structure. More rings could be assumed, for example four with strontium, but as already pointed out, these are unnecessary refinements as far as the orbits of the valence electron are concerned.

The expression for a as derived by Sommerfeld for a single ring (radius a_0) of electrons is given by Equation (31) where $k = 1$. The value of a^* is likewise determined by (31) where $k = 2$. This relation involves c_1 which is by Equation (26) proportional to $a^2{}_0$. We see, however, by Equation (46) that a_0 depends upon the nuclear charge and hence is different for Mg and Na, and other corresponding pairs of elements. This shrinkage of the ring when the nuclear charge increases by one unit must be considered in determining the ratio a^*/a. Now the addition of a second ring simply alters the value of c_1 in Equation (31).

Taking this into account as well as allowing for changes in the radii of the two rings as determined by Equation (48) we find:

$$\frac{a^*}{a} = 2\frac{\dfrac{p}{(Z^* - s_p)^2} + \dfrac{16}{(q + 2 - s_q)^2}}{\dfrac{p}{(Z - s_p)^2} + \dfrac{16}{(q + 1 - s_q)^2}}, \qquad (53)$$

where $Z^* = Z + 1$ is the atomic number of the alkali earth and Z is the atomic number of the alkali. For the doublet system of enhanced lines we use precisely the same formulae Equations (38) to (41) as for the arc spectra of the alkalis except that we replace s, p, d and b by the letters $\mathfrak{S}$, $\mathfrak{P}$, $\mathfrak{D}$ and $\mathfrak{B}$ respectively. Table VII shows the values of the empirically determined series constants. The last column gives the ratio a^*/a computed by Equation (53). This agrees with the empirical ratios, again substantiating our theory.

TABLE VII

RELATION BETWEEN a^* AND a

Elements	$a^* = \mathfrak{S}$	$a = s$	$a^* = \mathfrak{P}$	$a = p$	$a^* \div a$		
					$\mathfrak{S}/s$	$\mathfrak{P}/p$	Computed
Mg/Na.......	.93	.65	.30	.15	1.43	2.00	1.48
Ca/K.........	1.20	.82	.50	.29	1.46	1.72	1.49
Sr/Rb........	1.32	.81	.61	.36	1.63	1.70	1.66
Ba/Cs........	1.43	.95	.75	.45	1.50	1.66	1.66

We may therefore conclude that in all detail the enhanced spectrum of an alkali earth resembles the arc spectrum of the alkali of next lower atomic number. This relation may be extended to other pairs of elements. If we remove the valence electron from sodium the configuration is similar to that of neon, as seen from Table III. Hence the spark spectrum of sodium should resemble the arc spectrum of neon, and similarly for the other pairs of elements in these two groups. Such is observed, qualitatively, to be the case. Quantitative evidence is not at hand, since the series relations are as yet unknown for the spark

spectra of the alkalis and are not known at all completely for the rare gases. But both are alike in their complexity of structure. With these and a few other facts Kossel and Sommerfeld[30] proposed a general "displacement law" for spectra as summarized in Table VIII.

TABLE VIII

RELATION OF ARC AND SPARK SPECTRA

Group	VIII, 0	I	II	III	IV	V	VI	VII
Arc....	complex and triplets	doublet	triplet	doublet	triplet?	doublet?	triplet	?
Spark..	?	complex (and triplets?)	doublet	triplet	doublet?	triplet?	doublet?	triplet?

Where a question mark appears, the series relations have not been as yet untangled in the maze of spectral lines. The displacement law states that the spark spectrum of any simply ionized element resembles the arc spectrum of the element of next lower atomic number.

If an element loses two electrons its spectrum should be similar to the arc spectrum of the element of second lower atomic number. There is some indication of this second type of enhanced spectra in the spark spectra of carbon and of silicon, but nothing definite has been as yet established. The doubly ionized lithium atom should give a spectrum identical to hydrogen except that the important lines should lie in the extreme ultra-violet. The wave numbers should obey the approximate relation, analogous to Equation (9):

$$\nu = 9\,N_{\mathrm{Li}}\left(\frac{1}{n'^2} - \frac{1}{n^2}\right).$$

The series for which $n' = 1$, converges at $9\,N$ or about λ 101A, a spectral region of soft x-rays. Lines in series for higher values of n', which lie in the neighborhood of the visible spectrum, have at times been thought to have been detected in stellar spectra, but the evidence is not conclusive.

The spectrum of a negatively charged atom, one which has attached an extra electron, should resemble the arc spectrum of the element of next higher atomic number.

[30] Kossel and Sommerfeld, Verh. d. Phys. Ges., 21, pp. 240–59 (1919).

From the foregoing discussion it appears that the behavior of the elements as regards their spectra is analogous to that in radioactive transformations where the emission of an alpha particle gives rise to an element two steps to the left in the periodic table and the emission of a beta particle, an element one step to the right.

Spectroscopic Tables

Until recently there have been but three tables of wave-lengths available in which the lines have been correlated in series according to formulae of the Ritz or similar type; that of Dunz,[31] a supplement to Dunz's tables prepared by Lorenser[32] and these same tables arranged with a different notation in a book by Konen.[33] In these tables the numerical values of all the variable terms in series formulae are conveniently tabulated.

The notation employed by Dunz and Lorenser is that of Paschen. Paschen originally proposed for all the *ms* terms, half integer values for *m* such as 1.5 *s*, 2.5 *s* etc. Later it was found that the $\frac{1}{2}$ possessed no physical significance and hence more recent writers have included this factor in the series constant *a* of Equation (33). Whole numbers are therefore assigned to $n_a + n_r = m$, viz. 1 *s*, 2 *s* etc., just as has been always done with the *mp* and other variable terms. Also the variable term $m\Delta p$ used by earlier writers for the Bergmann series has been changed to *mb*. Accordingly the only modification necessary to the tables of Dunz and Lorenser, excluding errors, is the subtraction of $\frac{1}{2}$ from each value of *m* which refers to a *ms* or *mS* term and the substitution of *mb* for $m\Delta p$. However, since these tables were printed much more precise spectroscopic data have become available, especially in enhanced spectra which have been materially revised, and the entire subject has been brought up to the date April, 1921, by Fowler[34] in a book of nearly 200 pages, published March, 1922.

The vast quantity of data in this book was computed before the physical significance of the revised Paschen notation was appreciated. A notation is employed which is just enough different from the now generally preferred notation to be confusing to the beginner in this subject. The following table lists the essential differences between the revised Paschen notation which is employed in this book and Fowler's notation. One should familiarize himself with both notations; with the first in order to appreciate the physical significance on the basis of

[31] Dunz, Tübingen Dissertation, 1911.
[32] Lorenser, Tübingen Dissertation, 1913.
[33] Konen, "Das Leuchten der Gase und Dämpfe."
[34] See general reference 5 at end of chapter.

Sommerfeld's interpretation, with the second in order to obtain readily the numerical values from Fowler's tables.

Revised Paschen Notation	Fowler Notation
$1S,\ 2S$	$1S,\ 2S$
$2P,\ 3P$	$1P,\ 2P$
$3D,\ 4D$	$2D,\ 3D$
$1s,\ 2s$	$1s,\ 2s$ or $1\sigma,\ 2\sigma$
$2p,\ 3p$	$1p,\ 2p$ or $1\pi,\ 2\pi$
$3d,\ 4d$	$2d,\ 3d$ or $2\delta,\ 3\delta$
$4b,\ 5b$	$3f,\ 4f$ or $3\phi,\ 4\phi$
$1\mathfrak{S},\ 2\mathfrak{S}$	$1\sigma,\ 2\sigma$
$2\mathfrak{P},\ 3\mathfrak{P}$	$1\pi,\ 2\pi$
$3\mathfrak{D},\ 4\mathfrak{D}$	$2\delta,\ 3\delta$
$4\mathfrak{B},\ 5\mathfrak{B}$	$3\phi,\ 4\phi$

In Fowler's notation, singlet, doublet and triplet series are distinguished respectively by capital, Greek and small letter abbreviations. The ordinal numeral m, however, may be different from that in the revised Paschen notation. The following examples serve as illustrations.

Series	Notation	
	Revised Paschen	Fowler
Principal series of doublets of alkalis	$1s - mp,\quad m = 2, 3$	$1\sigma - m\pi,\quad m = 1, 2$
1st subordinate (diffuse) series of doublets of alkalis	$2p - md,\quad m = 3, 4$	$1\pi - m\delta,\quad m = 2, 3$
2d subordinate (sharp) series of doublets of alkalis	$2p - ms,\quad m = 2, 3$	$1\pi - m\sigma,\quad m = 2, 3$
Bergmann (fundamental) series of doublets of alkalis	$3d - mb,\quad m = 4, 5$	$2\delta - m\phi,\quad m = 3, 4$
Principal series of triplets of alkali earths	$1s - mp,\quad m = 3, 4$	$1s - mp,\quad m = 2, 3$
1st subordinate series of triplets of alkali earths	$2p - md,\quad m = 3, 4$	$1p - md,\quad m = 2, 3$
2d subordinate series of triplets of alkali earths	$2p - ms,\quad m = 1, 2$	$1p - ms,\quad m = 1, 2$
Principal series of singlets of alkali earths	$1S - mP,\quad m = 2, 3$	$1S - mP,\quad m = 1, 2$
Combination series of singlets of alkali earths	$1S - mp_2,\quad m = 2, 3$	$1S - mp_2,\quad m = 1, 2$
Principal series of doublets of ionized alkali earths	$1\mathfrak{S} - m\mathfrak{P},\quad m = 2, 3$	$1\sigma - m\pi,\quad m = 1, 2$
1st subordinate series of doublets of ionized alkali earths	$2\mathfrak{P} - m\mathfrak{D},\quad m = 3, 4$	$1\pi - m\delta,\quad m = 2, 3$
2d subordinate series of doublets of ionized alkali earths	$2\mathfrak{P} - m\mathfrak{S},\quad m = 2, 3$	$1\pi - m\sigma,\quad m = 2, 3$

These are merely some of the more striking differences in the notations. For the minor differences in the many combination series, reference must be made to the original tables. Throughout this book we shall refer to *fundamental* lines as those belonging to series converging at 1 *s*, 1 *S* or 1 𝔖. They are lines concerned with interorbital transitions for which one orbit represents the normal state of the unexcited atom. They are accordingly *fundamentally important* lines from the standpoint of atomic structure. Fowler and some other English and American writers use the term "fundamental" in reference to what we have called, following the German custom, the Bergmann series. While the latter nomenclature undoubtedly gives unwarranted credit to Bergmann it is preferred to the nomenclature "fundamental," since physically this series is quite remote from fundamental.

In the computation of series limits and variable terms Fowler employs the Hicks instead of the Ritz formula as follows:

$$(m, a) = \frac{N}{\left(m + a' + \frac{\alpha'}{m}\right)^2}. \qquad \text{(A)}$$

Referring to Equations (33) to (37), the variable term of the Ritz formula takes the form

$$(m, a) = \frac{N}{[m + a + \alpha c(m, a)]^2}. \qquad \text{(B)}$$

Carrying out the expansion involved by (m, a) in the denominator and dropping terms beyond m which are relatively small, especially when m is large, we obtain:

$$(m, a) = \frac{N}{\left[m + a + \frac{\alpha c N}{m^2}\right]^2}. \qquad \text{(C)}$$

On comparing this to (A) we note that since in (A) the ordinal number m occurs as the first power in the third term of the denominator while in (C) it occurs as the square, α' is not identical with αcN and a may differ somewhat from a'.

Since Fowler also uses different values of m, the numerical values of all variable series terms (m, a) will be very slightly different when computed by the two formulae. Fortunately the third term in the denominator is small, a correction term, so that these discrepancies are of little importance. A series line is always made up of the difference of two terms and is so computed that the difference is practically the same with each system of notation, since it must give the observed line. Limits

however are not observed, but are computed values, and accordingly depend somewhat upon the type of formula chosen. We may therefore expect to find small differences in series limits in tables computed in different manners. While these computed frequencies may be known to six significant figures *on the basis of a specified formula*, different formulae may disagree in the fifth figure or to even 10 parts in 50,000, and in certain cases where but few series terms are known, the differences may be very much greater.

In this book we are not concerned with computation of series limits but as will appear later we are interested in the actual physical value of convergence wave numbers regardless of the method whereby they are obtained. From this standpoint many of the limits listed in our tables are probably not certain by ten units. However, this small uncertainty is of negligible significance when referred to ionization potentials, energy levels in the atom, etc.[35]

In applying deductions from the theoretical derivation of the Ritz equation to values of the spectral series constants a and αc of Equation (B) as was done for example in Table VII, one should use the constants determined by the Ritz rather than by the Hicks equation. Even here however the differences are usually trivial when one considers that the theory in its present state is only qualitatively verified.

X-RAYS

One of the greatest successes of the quantum theory of spectroscopy is its application to the interpretation of x-ray spectra.[36] The characteristic x-ray spectra of an element may be grouped in series designated as the K, L, M, etc., series. The K radiation, which is of the shortest wave-length, is produced by an interorbital transfer where the final orbit is the inmost one in the atom. Figure 3 shows schematically how the various prominent x-ray lines are excited. $K\alpha$, the line of longest wave-length in the K series, is produced by an electron falling from the L ring to the K ring. $L\alpha$, the line of longest wave-length in the L series, is produced by an electron falling from the M ring to the L ring. The second line of the K series, $K\beta$, arises in a transition between the M and K rings. The limit of any series is the frequency determined by an electron falling from outside the atom into a vacant space in the

[35] Inconsistencies between the data given in the illustrations and tables, in this book, amounting to 5 or less units, may occur occasionally, since the latter have been revised in the proof to fit the latest available figures. These differences, however, are of little significance.
[36] See Chapter IX for detailed discussion.

corresponding ring. Since, as seen from Table III, the inner rings concerned with the production of x-rays all contain several electrons, the spectral series relations cannot be given by a simple formula of the Balmer type. It is necessary to consider the modifying effect of the other electrons in the various rings.

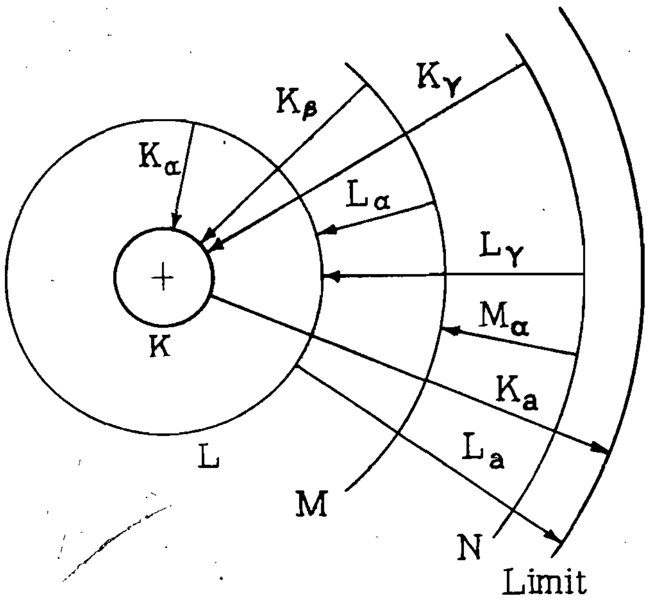


FIG. 3. Simple diagram showing prominent x-ray lines.

The $K\alpha$ line, for elements of atomic number 10 or greater, is probably the result of an interorbital transition represented as follows, where the figures and letters denote numbers of electrons in the groups specified

	K-ring	L-ring	M-ring
initial condition	1	8	r
final condition	2	7	r

By aid of Equations (50) and (51) we shall compute the total energy of the rings in the initial and in the final conditions.

Initial Condition: $W_p = -NhcZ^2,$ (54)

$$W_q = -2Nhc(Z - 3.80)^2, \tag{55}$$

$$W_r = -\frac{rNhc}{9}\left(Z - 9 - s_r\right)^2 \cdot \tag{56}$$

Final Condition: $$W_p = -2Nhc(Z - 0.25)^2, \quad (57)$$

$$W_q = -1.75Nhc(Z - 4.30)^2, \quad (58)$$

$$W_r = -\frac{r}{9}Nhc\left(Z - 9 - s_r\right)^2. \quad (59)$$

Subtracting the value of the total final energy from that of the total initial energy and equating this to $hc\nu$ we obtain:

For $K\alpha$ $$\frac{\nu}{N} = Z^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right) - 0.85\,Z + 3.6. \quad (60)$$

The first term in this expression is the simple formula representing the transition of an electron from orbit 2 to orbit 1, analogous to Equation (6) for hydrogen. The second and third terms are due to the disturbing action of the other electrons. While a formula derived in the above manner is of great interest if in only qualitative agreement with experiment, unfortunately this equation leaves much to be desired from the quantitative standpoint. The introduction of relativity considerations does not alter materially the computations for elements of low atomic number and the effect, here neglected, of the electrons in the outer rings on the energy of the inner rings, is also of a small order of magnitude. It is of interest to note that if in Equation (57) instead of $s_p = 0.25$ we arbitrarily put $s_p = 0.45$ we obtain:

For $K\alpha$ $$\frac{\nu}{N} = Z^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right) - 1.65\,Z + 3.88. \quad (61)$$

This relation agrees excellently with experiment as shown by Table IX.

TABLE IX

COMPUTATION OF ν/N FOR THE LINE $K\alpha$ FOR ELEMENTS OF LOW ATOMIC NUMBER

Element	Z	Computed ν/N	Observed ν/N
Na	11	76.5	76.6
Mg	12	92.1	92.0
Al	13	109.2	109.3
Si	14	127.8	128.0
P	15	147.9	148.0
S	16	169.5	170.0
Cl	17	192.6	193.4
K	19	243.3	243.8
Ca	20	270.9	271.3

Just as is the case with hydrogen and ionized helium where we find each line made up of several components, so with x-rays. Instead of the simple structure schematically indicated by Figure 3, many other x-ray lines are observed. A two-quantum L electron may move in either a circle or an ellipse. Likewise the M orbits of quantum number three may be either a circle or two types of ellipses. Hence we obtain doublet separations in the K and L spectra, due to the two forms of L orbits. The fine structure of x-ray lines, which is still more complicated than that just indicated, will be described in detail in Chapter IX. It is of interest here merely to mention the Sommerfeld derivation of the magnitude of the L-doublet separation as obtained from relativity considerations. The method is analogous to that used in deriving Equation (24) for the hydrogen doublet. Employing Equation (20) we compute the energy of a single electron for the orbit $n_a + n_r = 1 + 1$ and for the orbit $n_a + n_r = 2 + 0$. The difference in these energies is equal to $hc\Delta\nu$. One point must be noted, however, in that instead of the atomic number Z, we use $Z' = Z - z$. This is simply another method of correcting for the effect of the other electrons in the atom. For most of the elements $z = 3.50$, empirically determined, but it is evident that this is only an approximate method for representing nuclear defect and cannot be applied to elements of very low atomic number.

We accordingly obtain from Equation (20) the following relation in which the development is carried as far as the sixth power of the constant α.

$$\Delta\nu = NZ'^4\frac{\alpha^2}{2^4}\left[1 + \frac{5}{2}\frac{\alpha^2}{2^2}Z'^2 + \frac{53}{8}\frac{\alpha^4}{2^4}Z'^4 + \ldots\right]. \qquad (62)$$

Replacing $N\alpha^2$ by 16 $\Delta\nu_H$, Equation (24), we may compute the L-doublet separation for any element in terms of the separation of the hydrogen doublet. As an example, for uranium, $Z' = 92 - 3.50$, we find

$$\Delta\nu_U = 8.17 \cdot 10^7\,\Delta\nu_H = 2.98 \cdot 10^7 \text{ cm}^{-1}.$$

The observed doublet separation for uranium is $3.02 \cdot 10^7$ cm^{-1}, in excellent agreement with the above computed value which represents an extrapolation of eighty million-fold. We here see that the fine structure of the hydrogen Balmer lines is carried throughout the entire range of elements, appearing in their K and L x-ray spectra, on an increasingly greater scale of magnification as the atomic number progresses.

General References

(1) Bohr, Phil. Mag., 26, pp. 1, 476, 857 (1913); idem., 27, p. 506 (1914); idem., 29, p. 332 (1915); idem., 30, p. 394 (1915).

(2) Bohr, The Quantum Theory of Line Spectra, Parts I and II, Danish Academy of Science, 100 pp. (in English).

Series Spectra of the Elements, Zeit. Physik, 2, pp. 422–69 (1920).

Structure of Atoms and the Physical and Chemical Properties of the Elements, Zeit. Physik, 9, pp. 1–67 (1922).

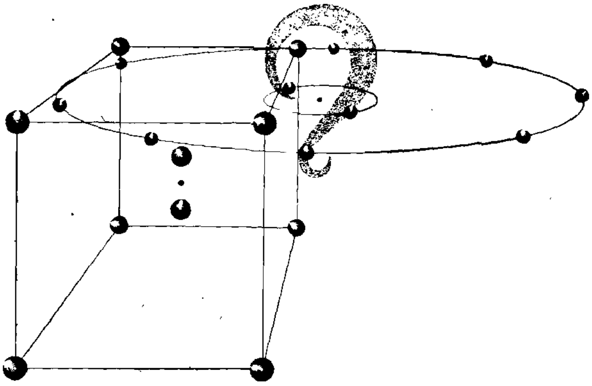
(3) Sommerfeld, Atomic Structure and Spectral Lines, 3d Edition, 764 pp. (1922).

(4) Silberstein, Report on the Quantum Theory of Spectra, 42 pp. (1920). A splendid synopsis of the theoretical development to this date.

(5) Fowler, Report on Series in Line Spectra, 183 pp. (1922). The most comprehensive catalog of series spectra ever published.

(6) Adams. The Quantum Theory, Bull. Nat. Res. Coun., 1, pp. 301–81 (1920).

(7) Page, Dynamic Theories of Atomic Structure, Bull. Nat. Res. Coun., 2, pp. 356–95 (1921).



Chapter II

Energy Diagrams

It is convenient to represent the various stationary states of a radiating atom by schematic diagrams. For example, in the case of hydrogen the total energy of the atom is a minimum when the electron is in the inmost orbit, total quantum number 1, as is evident from Equations (3), (17) or (20). When the electron is displaced to infinity, or just outside the sphere of influence of the core, which practically is a very small distance, the total energy is all potential and is a maximum. Between these two positions we have many orbits where the electron assumes intermediate values of the total energy corresponding to the total quantum numbers $n = 2, 3, 4$, etc. In general it is more convenient to consider instead of the total energy of the electron, the amount of work required to displace it from an inner to an outer orbit. Hence to the inmost orbit is ascribed the largest numerical value of the work, this being the work necessary to displace the electron to infinity. Such a diagram for hydrogen is shown in Figure 4. The first orbit, $n = 1$, corresponds to 215.6×10^{-13} ergs; the second to 53.9; the third to 23.95, etc. That is, it requires 215.6×10^{-13} ergs to completely remove the electron from its inmost stable position in the hydrogen atom, and 53.9×10^{-13} ergs to remove it from the second orbit, etc. The various series lines of hydrogen are shown on this diagram. For example H_α represents a transition from orbit 3 to orbit 2. Referring to the energy scale on the right we accordingly find that this represents an energy change of 3×10^{-12} ergs. (This value is obtained by taking the difference between the energy values corresponding to the head and tail of the arrow marked α. Note that *logarithms* of energy are plotted on the left in order to obtain an open scale.) Similarly the energy required to produce an emission of one quantum of any frequency represented by the series lines of hydrogen may be read from this plot. On the compressed scale of the diagram the fine structure of the various lines is not indicated. Actually orbit 2 is double and orbit 3 triple, as explained earlier in the text, cf. page 27.

Usually in such diagrams we are more concerned with the wave number ν of the radiation. It is accordingly desirable to plot instead of log energy the equivalent value of log ν. In this case the difference

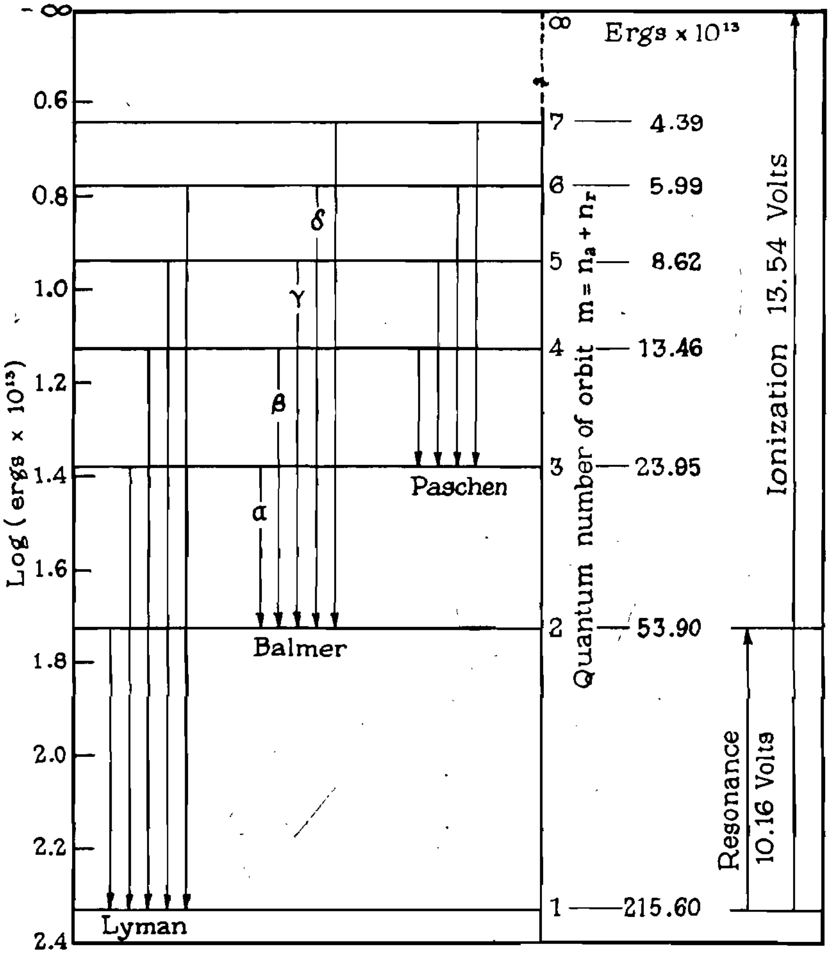


FIG. 4. Energy diagram for hydrogen.

in wave numbers corresponding to the initial and final orbits gives directly the wave number of the emitted radiation. Such a diagram for sodium is shown in Figure 5. All of the p-orbits are really double, but their separation is indistinguishable on this small scale of wave numbers.

Each D-line is represented by a transition from the initial 2 *p* orbit to the final 1 *s* orbit, and its wave number is given by the difference in wave numbers corresponding to these two energy levels 24472 or 24489 to 41449. Similarly for all other lines as far as shown on the

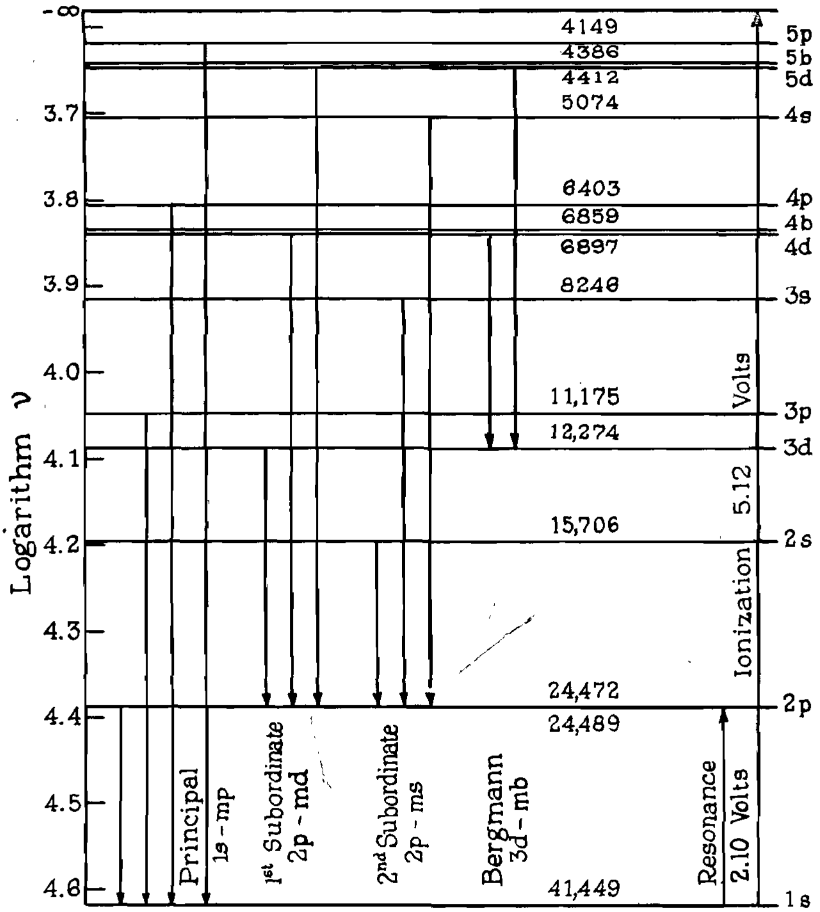


FIG. 5. Schematic representation of the arc spectrum of sodium.

plot (to the term 5 *p*). The first four lines of the principal series are indicated by arrows terminating at the convergence frequency 1 *s*, the electron falling from 2 *p*, 3 *p*, 4 *p*, 5 *p* respectively to 1 *s*. The first lines of the 1st and 2d subordinate series are indicated by arrows terminating at the convergence frequency of these two series. etc.

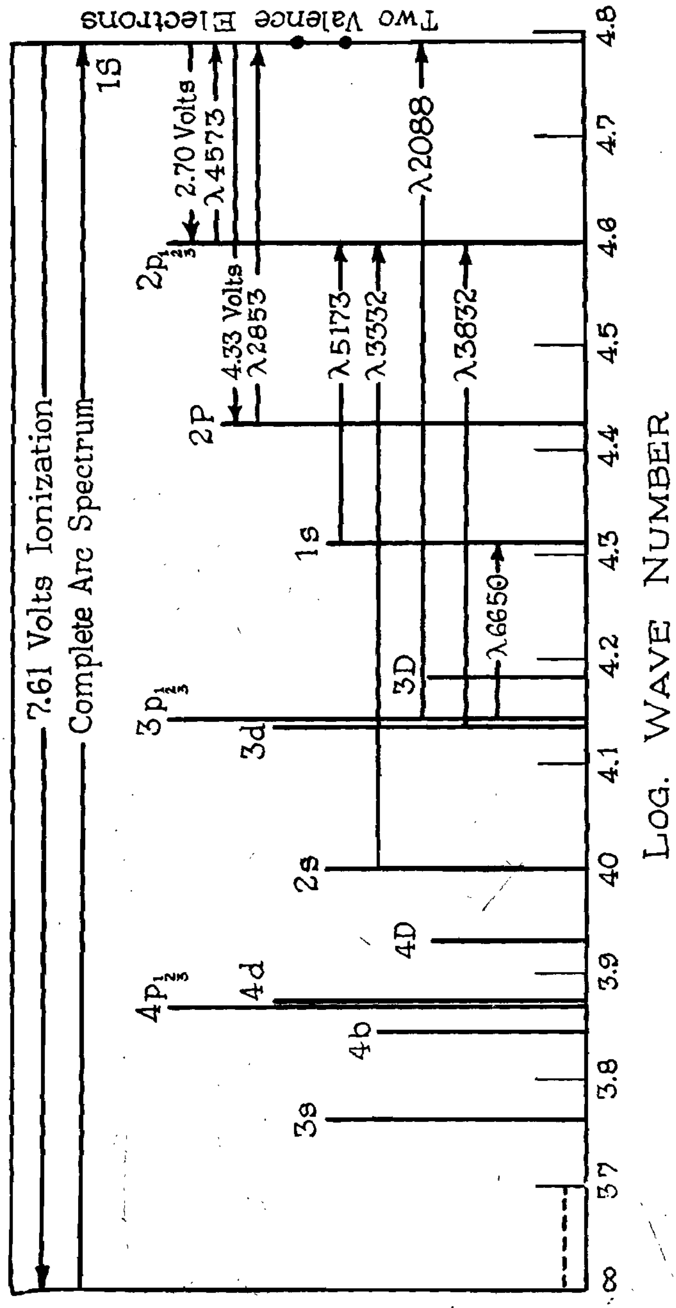


FIG. 6. Schematic representation of the arc spectrum of magnesium.

Figure 6 shows a similar diagram for the arc spectrum of magnesium, with several of the fundamental lines indicated by arrows. Making use of the quantum relation $hc^2\nu = eV \cdot 10^8$, we may express wave number in terms of the potential difference V through which an electron must freely fall in order to accumulate an amount of kinetic energy equivalent to a quantum of radiation of wave number ν. Expressed in volts we find:

$$\left.\begin{array}{l}\text{Volts} = V = 1.2345\,\nu \cdot 10^{-4} \\ \text{or} \qquad \nu = 8100\,V\end{array}\right\}. \tag{63}$$

Expressed in terms of wave-length λ measured in Angstrom units, we find:

$$V = 12345/\lambda. \tag{64}$$

The terminology "volts" by universal custom is used to signify a variety of meanings where the more precise statement of fact requires several words and is inconvenient. For example, instead of stating precisely that we refer to the velocity of an electron which has been accelerated through a potential difference of x volts, we may express this fact by stating that the electron has a velocity of x volts. Similarly, we may use the expression "an energy of x volts" meaning the value of the kinetic energy of the electron referred to above. With the quantum relation $hc^2\nu = eV \cdot 10^8$ tacitly understood, we may speak of frequencies, wave numbers and wave-lengths of x volts, meaning for example the wave number derived by substituting x for V in Equation (63), etc.[1]

In Figure 6, for example, a displacement of one electron to the left from 1 S to 2 p_2 requires 2.70 volts work. The electron in returning to 1 S gives up this energy as a quantum of radiation of wave-length 4573 A. The arrow-head shows the direction and end of the displacement in each case.

Figure 7 is a schematic representation of the enhanced lines of magnesium. It is noted that one of the valence electrons is absent, which fact greatly alters the values of the different energy or wave number levels. The first pair of each of the three series, Prin., 1 $\mathfrak{S}$ − m $\mathfrak{P}$, 1st Sub., 2 $\mathfrak{P}$ − m $\mathfrak{D}$, and 2d Sub., 2 $\mathfrak{P}$ − m $\mathfrak{S}$, is indicated by arrows.

The above examples illustrate the usefulness of such energy diagrams. All mathematically possible series and combination lines are given by the frequency differences of pairs of energy levels. The various levels,

[1] Language serves two purposes; one in a definitional sense, where preciseness is requisite; the other for the conveyance of ideas, where conciseness is essential. It is in the latter sense that the above inexact yet unambiguous notation is justifiable.

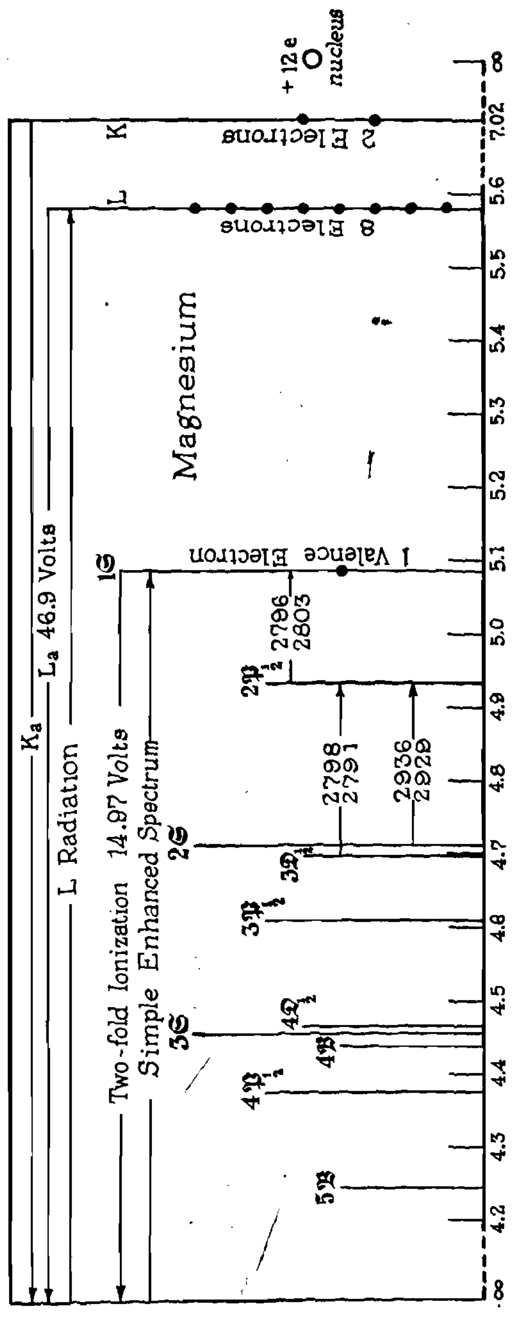


Fig. 7. Schematic representation of the spark spectrum and x-ray limits of *magnesium*.

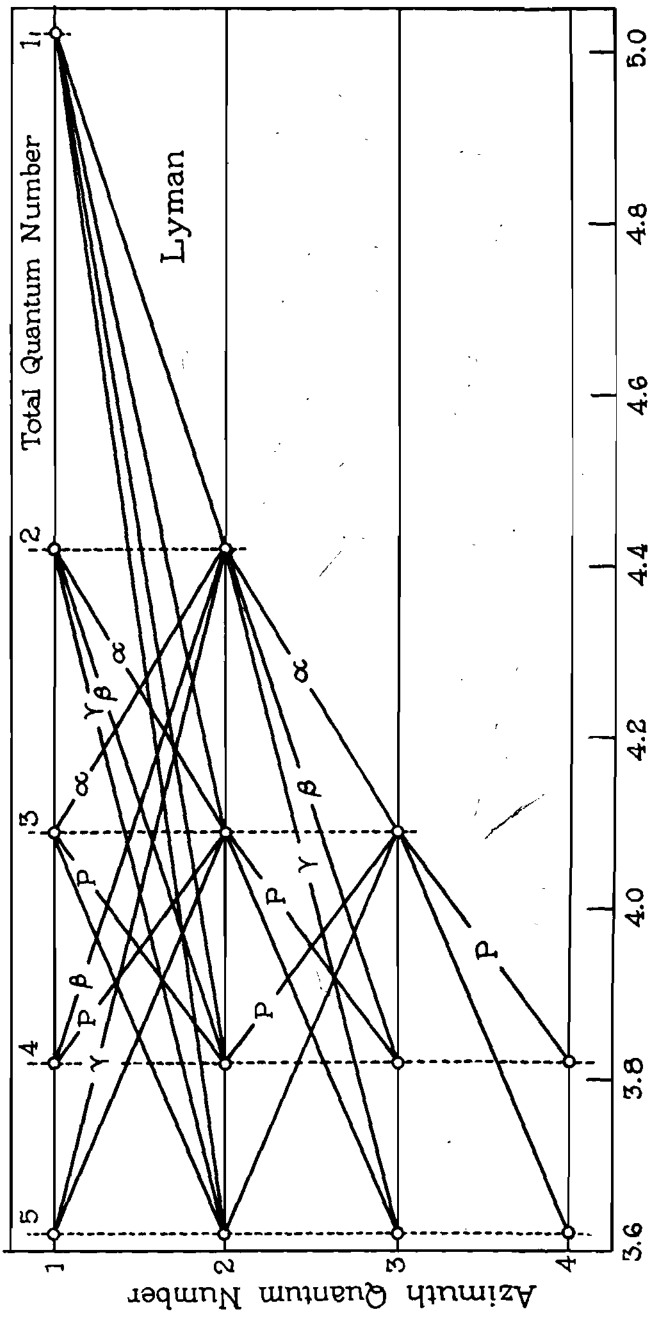


FIG. 8. Diagrammatic representation of series relationships for hydrogen.

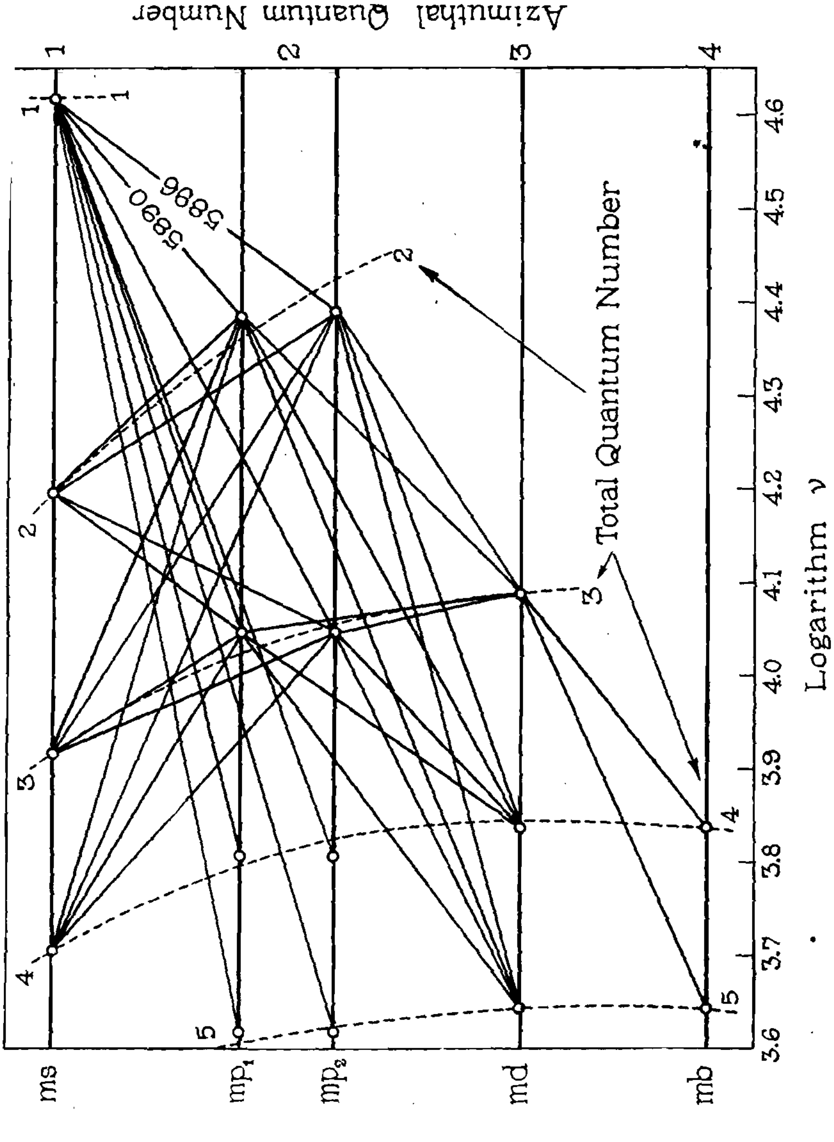


FIG. 9. Diagrammatic representation of series relationships for sodium.

however, are concerned with only the total quantum number. No differentiation between azimuthal and radial quantum numbers is made. The so-called Grotrian diagrams remedy this difficulty. These possess the additional advantage that the fine structure, doublets, etc., may be readily indicated.

Figure 8 is such a diagram for hydrogen. Three coördinates are employed: as abscissa, logarithm of the wave number; as ordinate, the azimuthal quantum number; and a third system, indicated by dotted lines, the sum of the azimuthal and radial quantum numbers. Each point shown by a small circle represents a wave number or equivalent energy level which may be computed from Equation (20) by the proper assignment of azimuthal and radial quantum numbers. A spectral frequency is indicated by a straight line between two points and its numerical value is given by the difference in the wave numbers corresponding to each end of this line. By the Bohr principle of selection the change in azimuthal quantum number $= \pm 1$. Hence all straight lines representing spectral frequencies must terminate in adjacent horizontal lines of constant azimuthal quantum number. The group terminating at the upper right-hand point represents the Lyman series, each member of which is a singlet. The plot shows H_α and H_β of the Balmer series, each member being a triplet and hence appearing three times. The first line of the Paschen series, which is a quintuplet, appears five times on the chart, and is designated by the letter *P*.

In a similar manner the spectra of the heavier elements may be illustrated. Figure 9 represents sodium. The double *mp* terms, all having the same azimuthal quantum number 2, are shown by mp_1 and mp_2. All lines representing the principal series terminate at the upper right-hand point and each occurs twice on account of the double-*p* values. The two D-lines are marked with their proper wave-lengths. The straight lines representing the 1st and 2d subordinate series all terminate at 2 *p* and again occur twice because of the double values of *mp*. The above discussion illustrates the use and construction of these diagrams for representing series relations. We shall have occasion to refer to them subsequently.

Chapter III

Ionization and Resonance Potentials for the Elements

When electrons are accelerated through gas or vapors there are, especially for monatomic gases having a small electron affinity and the metallic vapors, well-defined critical velocities at which a large transfer of energy takes place between electrons and atoms. For velocities below this minimum critical value the collision is elastic. the electron rebounding from the atom with usually an alteration in its direction of path but with the same kinetic energy. In general two types of inelastic collision occur, one in which an outer electron of the atom undergoes an interorbital transition, and the other in which an outer electron is completely removed. In the latter case the atom is "simply" ionized, having a total net charge $+ e$. The potential through which an electron must fall in order to accumulate just sufficient velocity to produce the first type of inelastic collision has been termed by Tate and Foote the resonance potential. The corresponding value for a collision resulting in ionization is known as the ionization potential. In general there may be several ionization potentials corresponding to the removal of 1, 2, 3, etc. electrons, but only simple ionization will be considered in the present section. Experimental evidence has shown that the loss in kinetic energy of the impacting electron during a collision of the "resonance" type is equal to the resonance potential, whether the initial energy be exactly equal to or greater than that corresponding to the resonance potential. Whether or not this be true in the case of ionization remains to be demonstrated, for it is possible that the ejected electron may leave the atom with any velocity whatever, depending upon the nature of the impact.

Since energy is abstracted from the impacting electron and absorbed by the atom, the total energy of the *atom*, following a collision, is increased by an amount equivalent to either the resonance or ionization potential. When the atom subsequently returns to its normal state this energy is emitted in the form of radiation. In the case of ionization the electron may return by a variety of interorbital transitions, each resulting

in an emission of a quantum of wave number ν_k, subject to the conservation of energy condition:

$$\Sigma hc^2\nu_k = eV_i \cdot 10^8,$$

where V_i is the ionization potential. With numerous atoms and electrons returning to equilibrium in different manners, we have as the composite result an emission of the complete arc spectrum. If an electron returns to the normal orbit directly without passing through intermediate states of equilibrium, but one frequency is emitted, which is the highest frequency in the arc spectrum. This frequency, as is evident from a consideration of the energy diagrams Figures 4 to 9 and Equations (34) to (37), is the highest convergence frequency of any series of the arc spectrum, the wave numbers 1 *s* for the alkalis and 1 *S* for the metals of Group II of the periodic table. In the normal unexcited atom, accordingly, the outer electron concerned with emission of spectral lines lies in the 1 *s* or 1 *S* orbit.

The energy absorbed by the atom at the resonance potential is not great enough to completely eject an electron, but rather is just sufficient to displace it to a neighboring orbit of higher energy value. We have found experimentally that the alkali metals possess a resonance potential corresponding exactly to the amount of work required to displace an electron from the 1 *s* orbit to the 2 *p* orbit, the first energy level above 1 *s*. For sodium, as illustrated by Figure 5, the energy absorbed by the atom is 2.10 volts. The electron accordingly in returning to its normal orbit releases this amount of energy as a quantum of radiation of wave number $\nu = 1\ s - 2\ p$; that is, the D-lines and no other lines of the sodium spectrum are emitted. Since both D-lines are emitted it may be expected that two resonance potentials exist, but if so the difference in their values would be many times less than our errors of measurement. It is doubtful whether any conclusion in this regard may be drawn from the fact that we found a single resonance potential for caesium where the doublet separation is considerably larger. There is on the other hand a vague possibility that the component of higher frequency is the determining factor for the resonance potential, in rather superficial analogy to the excitation of the *K* series at the minimum potential corresponding to *Ka*.

In the case of the metals of Group II of the periodic table the authors have found that two resonance potentials exist. One of these corresponds to the energy required to displace an electron from its normal position in the 1 *S* orbit to the neighboring orbit 2 p_2. The electron in

returning to the 1 S orbit gives up this energy as a quantum of radiation of wave number $\nu = 1\ S - 2\ p_2$. Only the single line is emitted. In fact the corresponding frequencies $1\ S - 2\ p_1$ and $1\ S - 2\ p_3$ are absent even in the complete arc spectra of these metals. The reason for these missing terms is explained, not at all satisfactorily, however, by Sommerfeld's theory of "internal quantum numbers" and is beyond the scope of the present book.[1]

TABLE X

RESONANCE AND IONIZATION POTENTIALS, GROUP I

Element	Z	Series Notation	ν	Volts	
				Computed	Observed
Li	3	$1\ s$	43,486	5.368	
		$1\ s - 2\ p_1$	14,903	1.840	
Na	11	$1\ s$	41,449	5.116	5.13
		$1\ s - 2\ p_1$	16,973	2.095	2.12
K	19	$1\ s$	35,006	4.321	4.1
		$1\ s - 2\ p_1$	13,043	1.610	1.55
Cu	29	$1\ s$	62,308	7.692	
		$1\ s - 2\ p_1$	30,784	3.800	
Rb	37	$1\ s$	33,689	4.158	4.1
		$1\ s - 2\ p_1$	12,817	1.582	1.6
Ag	47	$1\ s$	61,096	7.542	
		$1\ s - 2\ p_1$	30,473	3.762	
Cs	55	$1\ s$	31,405	3.877	3.9
		$1\ s - 2\ p_1$	11,732	1.448	1.48
Au	79	$1\ s$	70,000?	8 to 9?	
		$1\ s - 2\ p_1$	41,174	5.1	

The second resonance potential corresponds to the energy required to displace an electron from its normal position in the 1 S orbit to the 2 P orbit. If the electron returns directly to the 1 S orbit without passing

[1] Sommerfeld, "Atombau," 3d Ed., Chap. 6, Section 5.

through intermediate states of equilibrium, this energy is liberated as a quantum of radiation of wave number $\nu = 1\,S - 2\,P$. These transitions are illustrated in the case of magnesium by Figure 6, the resonance potentials being 2.70 and 4.33 volts.

In general we note that the ionization potential of a monatomic vapor corresponds to the highest convergence frequency in the arc spectrum of the material; to the limit of a series the first line of which corresponds to a resonance potential. Exceptions to this general rule will be given individual attention later. As will be considered in more detail under a separate section[2] these series are absorption lines for the normal atom, so that ionization and resonance potentials in certain cases may be predicted from a knowledge of the prominent absorption lines.

Group I: Table X shows the ionization and resonance potentials for metals in Group I of the periodic table. The computed values are obtained from the series relationships and are to be preferred to our direct experimental values for all computations in which a consideration of ionization and resonance potentials enters. No satisfactory results have been obtained with copper, silver and gold, although we have made very elaborate and extensive experiments. The difficulty is of a pyrometric nature, temperatures of 2000° C and a high vacuum being required. However, from series relationships and a consideration of the absorption or "reversed" lines the computed values are probably correct.

Group II: Table XI shows the computed values of the resonance and ionization potentials for elements of Group II of the periodic table, together with the experimental values obtained by the authors.[3]

Group III: The series relations in this group, which includes aluminum, gallium, indium, and thallium, should be similar to that of the alkali metals. The arc lines have been beautifully correlated in series of this type, consisting of widely spaced doublets, but the convergence frequency of the principal series is smaller than that of the subordinate series — a fact not easily reconciled with the quantum theory unless the observed principal series is of a second type converging at 2 s instead of 1 s. This would indicate that the most important principal series which converges at 1 s is as yet undiscovered. If so most of the lines except the first term should lie in the extreme ultra-violet. It is of interest that several lines supposedly of the arc spectrum have been observed which have a greater wave number than the highest known

[2] Cf. Chapter IV.

[3] For data by other observers, see general references at end of chapter. Several of the experimental values in Tables X and XI were obtained by Tate and Foote.

convergence frequency, again indicating that 1 *s* remains to be discovered.[4]

TABLE XI

RESONANCE AND IONIZATION POTENTIALS, GROUP II

Element	Z	Series Notation	ν	Volts	
				Computed	Observed
Be	4		> Mg ?	> Mg ?	
Mg	12	$1\,S$	61,672	7.613	7.75
		$1\,S - 2\,p_2$	21,871	2.700	2.65
		$1\,S - 2\,P$	35,051	4.327	4.42
Ca	20	$1\,S$	49,305	6.087	6.01
		$1\,S - 2\,p_2$	15,210	1.878	1.90
		$1\,S - 2\,P$	23,652	2.920	2.85
Zn	30	$1\,S$	75,767	9.353	9.3
		$1\,S - 2\,p_2$	32,502	4.012	4.18
		$1\,S - 2\,P$	46,745	5.771	5.65
Sr	38	$1\,S$	45,926	5.670	
		$1\,S - 2\,p_2$	14,504	1.791	
		$1\,S - 2\,P$	21,698	2.679	
Cd	48	$1\,S$	72,539	8.955	8.92
		$1\,S - 2\,p_2$	30,656	3.784	3.95
		$1\,S - 2\,P$	43,692	5.394	5.35
Ba	56	$1\,S$	42,029	5.188	
		$1\,S - 2\,p_2$	12,637	1.560	
		$1\,S - 2\,P$	18,060	2.230	
Hg	80	$1\,S$	84,178	10.392	10.2
		$1\,S - 2\,p_2$	39,413	4.866	4.76
		$1\,S - 2\,P$	54,066	6.674	6.45
Ra	88	$1\,S$	40–50000?	5–5.5?	
		$1\,S - 2\,p$ [illegible]	12,500?	1.5?	

The only critical potentials known for this family are our measurements on thallium, which are rather unsatisfactory. We found a resonance potential 1.07 volts and an ionization potential 7.3 volts. The resonance potential corresponds closely to the component of higher frequency of the first pair of Paschen's principal series usually given as $\nu = 1\,s - 3\,p_1$ but which more likely should have the notation $\nu = 2\,s - 3\,p_1 = 8683.3 \approx 1.07$ volts. This exact agreement with experiment is accidental, and in case this frequency is $2\,s - 3\,p_1$, it probably has no physical significance whatever, as the determining wave number then should be $1\,s - 2\,p_1$. The observed ionization potential corresponds to a value of 1 *s* of about the magnitude to be expected but greater than any convergence frequency known at present. More observations on critical potentials for this group should be made; our work on thallium should be repeated with greater care; and the spectral series relations should be further investigated with the object of finding higher convergence frequencies for the principal series of all the metals of this family.

Group IV: The series relations for this family are in a very unsatisfactory state,[5] and there is little hope for directly determining the critical potentials of such highly refractory elements, except lead, unless an entirely new method of experimentation should be devised. We have tried without success the vaporization of such refractory materials in a high vacuum, using a small crucible and projecting an approximately unidirectional stream of the vapor through the ionization chamber. The problem is most difficult both from the standpoint of electrical measurements and of pyrometry. Our results with lead by the usual method gave for the resonance potential 1.26 volts and for the ionization potential 7.93 volts. The first point coincides with an isolated group of infra-red lines, observed by Randall, the shortest wave-length of which is $\lambda = 10291 \approx 1.30$ volts.

Group V: Series relations are unknown[6] and it is questionable whether measurements on critical potentials of polyatomic vapors give any direct indication of spectral frequencies of line series since the work of ionization, for example, may include that of dissociation of the molecule into atoms.[7] It is even possible that the *band* spectra of polyatomic vapors are more closely related to the values indicated

convergence frequency, again indicating that 1 *s* remains to be discovered.[4]

TABLE XI

Resonance and Ionization Potentials, Group II

Element	Z	Series Notation	ν	Volts	
				Computed	Observed
Be	4		> Mg ?	> Mg ?	
Mg	12	$1S$ $1S-2p_2$ $1S-2P$	61,672 21,871 35,051	7.613 2.700 4.327	7.75 2.65 4.42
Ca	20	$1S$ $1S-2p_2$ $1S-2P$	49,305 15,210 23,652	6.087 1.878 2.920	6.01 1.90 2.85
Zn	30	$1S$ $1S-2p_2$ $1S-2P$	75,767 32,502 46,745	9.353 4.012 5.771	9.3 4.18 5.65
Sr	38	$1S$ $1S-2p_2$ $1S-2P$	45,926 14,504 21,698	5.670 1.791 2.679	
Cd	48	$1S$ $1S-2p_2$ $1S-2P$	72,539 30,656 43,692	8.955 3.784 5.394	8.92 3.95 5.35
Ba	56	$1S$ $1S-2p_2$ $1S-2P$	42,029 12,637 18,060	5.188 1.560 2.230	
Hg	80	$1S$ $1S-2p_2$ $1S-2P$	84,178 39,413 54,066	10.392 4.866 6.674	10.2 4.76 6.45
Ra	88	$1S$ $1S-2p_2$ $1S-2P$	40–50000? 12,500? 20,700?	5–5.5? 1.5? 2.6?	

[4] These are conveniently summarized in tables by Fowler, "Report on Series in Line Spectra," Chap. 17.

The only critical potentials known for this family are our measurements on thallium, which are rather unsatisfactory. We found a resonance potential 1.07 volts and an ionization potential 7.3 volts. The resonance potential corresponds closely to the component of higher frequency of the first pair of Paschen's principal series usually given as $\nu = 1\ s - 3\ p_1$ but which more likely should have the notation $\nu = 2\ s - 3\ p_1 = 8683.3 \simeq 1.07$ volts. This exact agreement with experiment is accidental, and in case this frequency is $2\ s - 3\ p_1$, it probably has no physical significance whatever, as the determining wave number then should be $1\ s - 2\ p_1$. The observed ionization potential corresponds to a value of $1\ s$ of about the magnitude to be expected but greater than any convergence frequency known at present. More observations on critical potentials for this group should be made; our work on thallium should be repeated with greater care; and the spectral series relations should be further investigated with the object of finding higher convergence frequencies for the principal series of all the metals of this family.

Group IV: The series relations for this family are in a very unsatisfactory state,[5] and there is little hope for directly determining the critical potentials of such highly refractory elements, except lead, unless an entirely new method of experimentation should be devised. We have tried without success the vaporization of such refractory materials in a high vacuum, using a small crucible and projecting an approximately unidirectional stream of the vapor through the ionization chamber. The problem is most difficult both from the standpoint of electrical measurements and of pyrometry. Our results with lead by the usual method gave for the resonance potential 1.26 volts and for the ionization potential 7.93 volts. The first point coincides with an isolated group of infra-red lines, observed by Randall, the shortest wave-length of which is $\lambda = 10291 \simeq 1.30$ volts.

Group V: Series relations are unknown[6] and it is questionable whether measurements on critical potentials of polyatomic vapors give any direct indication of spectral frequencies of line series since the work of ionization, for example, may include that of dissociation of the molecule into atoms.[7] It is even possible that the *band* spectra of polyatomic vapors are more closely related to the values indicated by critical potentials. In Table XII the potentials for antimony and

[5] Fowler summarizes the present meager knowledge of the series spectra of these elements in two pages, loc. cit., pp. 163–4.
[6] Fowler, loc. cit., p. 164.
[7] See latter part of Chap. VIII.

bismuth are unreliable. Although we have made numerous determinations each one of which appeared satisfactory by itself, the different observations showed wide deviations, possibly accounted for by the formation of polarization films on the electrodes. It should be pointed out that observations on ionization potentials without corresponding data on resonance, for velocity corrections, are of little value *with non-metallic vapors*, as surprisingly large errors arise in "initial velocities" determined by the usual velocity distribution curves. Such is not the case with metallic vapors and the rare gases.

TABLE XII

RESONANCE AND IONIZATION POTENTIALS, GROUP V

Element	Z	Observed Potential, Volts		Remarks
		Resonance	Ionization	
N	7	8.18	16.9	Lines at λ 1494.8 and λ 1492.8 = 8.27 volts. Ionization at 17.75, 25.4, 30.7 observed by Brandt.[8]
P	15	5.80	13.3	
As	33	4.7	11.5	
Sb	51	?	7.8–8.5	Uncorrected for initial velocity.
Bi	83	2.0	8.0–8.5	

Group VI: Our knowledge of the spectral series of these elements[9] is confined to oxygen, sulphur and selenium. Principal, 1st and 2d subordinate series of both single lines and triplets are known for oxygen, and a similar triplet structure for sulphur and selenium. There is no apparent relation between the values of the series terms and the observed critical potentials. For example, Fowler lists 1 S and 1 s for oxygen as $\nu = 33043$ and $\nu = 36069$ respectively, corresponding to roughly four volts, whereas the ionization potential is nearly sixteen volts. This

[8] Brandt, Z. Physik, 8, pp. 32–44 (1921). For data on nitrogen by other observers see Hughes, general references at end of chapter.
[9] Fowler, loc. cit., p. 166.

lack of agreement might be due to the fact that the wave number ν = 33043 is really 2 S instead of 1 S and that 1 S is as yet unknown. On the other hand it is more probable that the ionization potential is characteristic of the molecule, as above mentioned, and hence has only a remote relation to spectral frequencies for the atom. Table XIII summarizes our data on several of the polyatomic elements in this group. The values for selenium and for tellurium are questionable.

TABLE XIII

RESONANCE AND IONIZATION POTENTIALS, GROUP VI

Element	Z	Observed Potential Volts		Remarks
		Resonance	Ionization	
O	8	7.91	15.5	See Hughes [10] for data by other observers.
S	16	4.78	12.2	
Se	34	3.0–3.5	12–13	(12.7 observed by Udden.)[11]
Te	52	2.3–2.9	?	

Group VII: Spectral relations unknown.[12] Hughes and Dixon[13] observed a critical potential in chlorine at 8.2 volts and in bromine at 10.0 volts, but whether these are ionization or resonance potentials is uncertain. For iodine we have found a resonance potential of 2.34 ± 0.2 volts and an ionization potential of 10.1 ± 0.5 volts. Smyth and Compton[14] observed ionization of molecule at 9.4 volts, ionization of atom at 8.0 volts and ionization of fluorescing molecule at 6.8 volts.

Saha, *Nature, 107*, p. 683 (1921), states that Catalan in some unpublished work has found 1 S for manganese. His value gives 7.38 volts for the computed ionization potential, which is consistent with the behavior of the element in the solar spectrum, as mentioned on page 172.

Groups VIII & 0: Table XIV summarizes mainly the work of Horton and Davies[15] on the rare gases, work which has been done apparently

[10] See general references at end of chapter.
[11] Udden, Phys. R., 18, p. 385 (1921).
[12] Fowler, loc. cit., p. 173, summarizes some data on manganese triplets.
[13] Hughes and Dixon, Phys. R., 10, p. 495 (1917).
[14] *Smyth and Compton, Phys. R., 16, pp. 501–13 (1920).*
[15] Horton and Davies, Proc. Roy. Soc., 95, p. 408 (1919); 97, p. 1 (1920); 98, p. 121 (1920); *Phil. Mag., 39, p. 592 (1920).*

with high precision and the greatest experimental skill. The data of these and other observers are tabulated by Hughes.

TABLE XIV

RESONANCE AND IONIZATION POTENTIALS, GROUP 0

Element	Z	Observed Potential Volts		
		Resonance	Ionization	
He	2	20.4	25.6	
		21.2	(25.4	Franck and Knipping[16] later 25.3)
			(25.5	Compton [17])
Ne	10	11.8	16.7	
		17.8	20.0	
			22.8	
A	18	11.5	15.1	

No data on the metals exist either in regard to spectral series[18] or critical potentials.

Hydrogen. Hughes lists the work of eleven groups of experimenters. In Table XV we summarize the values obtained by Horton and Davies[19] and by ourselves.[20]

TABLE XV

RESONANCE AND IONIZATION POTENTIALS, HYDROGEN

Resonance		Ionization		Observers
1st	2d	1st	2d	
10.5	13.9	14.4	16.9	Horton and Davies
10.4	12.0	13.3	16.0	Mohler and Foote (Revised from more recent data. Earlier published values were 12.2 and 16.5)

[16] Franck and Knipping, Zeit. Physik, 1, p. 320 (1920).
[17] Compton, Phil. Mag., 40, p. 553 (1920).
[18] Constant difference groups are known, suggesting that series relations exist.
[19] Proc. Roy. Soc., 97, p. 23, 1920.
[20] Mohler and Foote, Bur. Standard Sci. Paper, 400; Phys. R., 19, pp. 419–20 (1922).

THE NORMAL HELIUM ATOM

While the quantum theory yields results of the greatest precision in the case of ionized helium, a satisfactory interpretation of the normal helium atom with two electrons proves to be very difficult. The simple Bohr theory assumed that the two electrons revolved in a single circular orbit about the nucleus of charge $+ 2\,e$. By Equation (50) we obtain accordingly for the total energy of the atom:

$$W = -2\frac{Nhc}{1^2}(2 - 0.25)^2 = -1.321 \cdot 10^{-10}\,ergs \Leftrightarrow -83.0\,\text{volts}. \quad (65)$$

The energy of the simply ionized atom is obtained by the same equation or by Equation (20) and gives directly the value -54.2 volts concerning which there can be no question, as it is derived from the solution of the simple problem of two bodies which has been amply developed and verified in the earlier part of this book. The difference in these two values, $83.0 - 54.2 = 28.8$ volts, should give the ionization potential of helium, whereas by direct experiment we find about 25.5 volts, a sufficiently unsatisfactory agreement to warrant the rejection of this structure for the normal helium atom. Furthermore it is not in accord with the known diamagnetic properties of helium.

Helium[21] possesses two independent groups of series in its arc spectrum, a single line and a doublet system, between which no combinations whatever occur. This peculiar behavior immediately suggests that the systems arise in two entirely different configurations of the helium atom. In fact it was once thought that helium must be a mixture of two gases, for convenience called orthohelium and parhelium, names now retained to denote the two types of atomic configuration.

Figure 10 shows the series relations for helium. The upper half represents the single-line system ascribed to parhelium. The lower half of the figure shows the doublet system of orthohelium. The doublets are exceedingly close and hence do not appear resolved in this diagram. In the notation we represent, as usual, singlet series by capital letters and doublet series by lower case letters. The highest convergence limits 2 S and 2 s for these two groups correspond respectively to 3.954 and 4.747 volts. If either of these states represented the normal atom, one of the values named should be the ionization potential, and the stability of the atom would be but 1/7 the observed stability. The most obvious step accordingly is to identify the normal state with either 1 S or 1 s, to which should correspond the experimental value for the ionization potential.

[21] Fowler, loc. cit., p. 89.

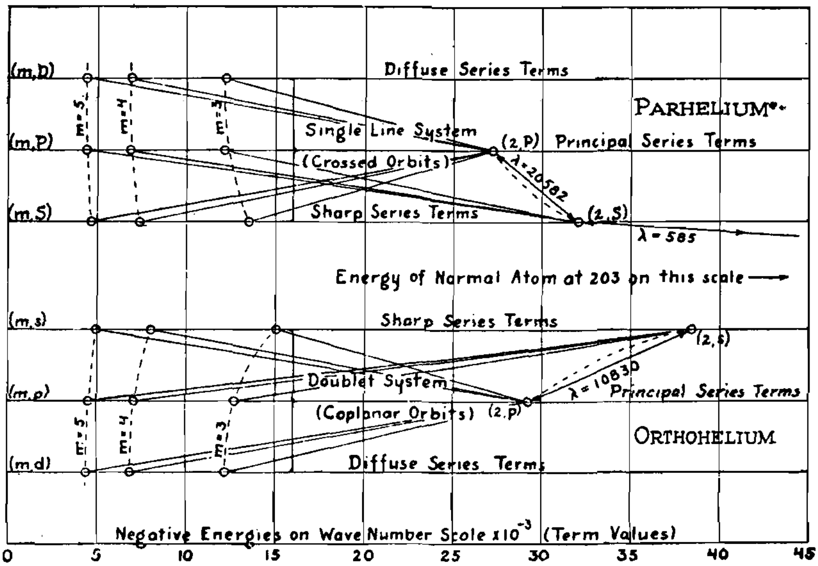


FIG. 10. The series relationships for helium. (From Kemble, Phil. Mag. 42, p. 124; 1921.)

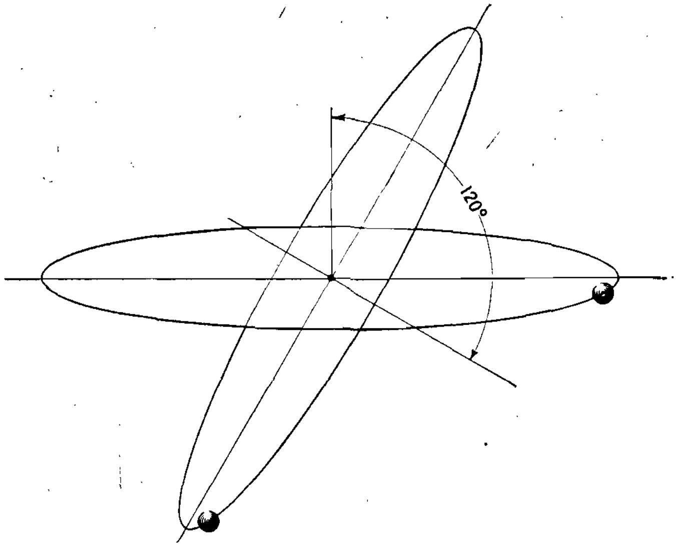


FIG. 11. The normal helium atom.

The first electron bound to the helium nucleus revolves in a 1 quantum circular orbit. The second electron cannot in the normal state revolve in a coplanar orbit which surrounds the first because (a) the readily computed energy relations are not in agreement with ionization potential measurements and (b) the configuration would resemble lithium and should have a positive valence. As already mentioned (cf. discussion of Equation (65)), the two electrons cannot revolve in the same orbit, and as Bohr points out there is no type of transition conceivable between a state where the electrons occupy different orbits and that state in which the same orbit is occupied.

Bohr[22] concludes that in the normal state both electrons move in 1 quantum paths which make an angle of 120 degrees with each other as shown in Figure 11. To a first approximation these are circular orbits. On account of the mutual action of the two electrons, however, there is a slight deviation from the true circle, and the two orbits rotate slowly about the fixed axis of angular momentum of the atom. Bohr states that while the mathematical analysis of this three-body problem is not yet complete, preliminary computations indicate that it will give the correct value of the ionization potential.

Lande[23] has shown that the single-line system belongs to a crossed-orbit configuration, where one of the electrons undergoes interorbital transitions, while the doublet system arises in transitions of the outer electron in a coplanar configuration. We accordingly assign the singlet spectra to parhelium and the doublet spectra to orthohelium. Normal helium is therefore the 1 *S* state of parhelium. In the 2 *s* state of orthohelium the inner electron revolves in a 1 quantum circular orbit, while the outer electron, according to Bohr, moves in a coplanar elliptical orbit of total quantum number 2 and azimuthal quantum number 1. The 1 *s* state should therefore require two electrons in the same circular orbit at opposite ends of a diameter. Although this is the most stable type of configuration, Bohr, as stated above, concludes it cannot be formed, and accordingly we have no term 1 *s* in the helium spectrum, a hypothesis also advanced by Franck and Reiche[24] from other considerations.

Since Bohr's mathematical computations on the dynamics of these systems have not been published, we shall, following Franck and Knipping,[25] compute 1 *S* from their observation on the ionization potential.

[22] Bohr, Z. Physik, 9, pp. 1–67 (1922).
[23] Physik. Z., 20, pp. 228–34 (1919); 21, pp. 114–22 (1920).
[24] Z. Physik, 1, pp. 154–160 (1920).
[25] Z. Physik, 1, p. 320 (1920).

One obtains $1\ S = 202910 \approx 25.3$ volts. Using the spectroscopically determined values of $2\ S$ and $2\ s$, as shown in Figure 10, we find

$$1\ S - 2\ S = 202910 - 32031 = 170880 \approx 21.1 \text{ volts}$$

$$1\ S - 2\ s = 202910 - 38453 = 164460 \approx 20.6 \text{ volts}$$

These potentials correspond to the resonance potentials of helium, the observed values of which are 21.2 and 20.4 volts, as given in Table XIV. It therefore appears that a 21.1 volt impact ejects an electron from the normal $1\ S$ state to the $2\ S$ state of parhelium, while a 20.6 volt impact ejects an electron from the normal $1\ S$ state of the crossed orbit system to the $2\ s$ state of the coplanar system, orthohelium.

The existence of the wave number $1\ S$ immediately suggests the presence of a principal series of the form $1\ S - mP$ the first few terms of which may be computed from the known values of mP as follows:

Notation	ν	λ
$1\ S - 2\ P$....................	175,730	569 A
$1\ S - 3\ P$....................	190,810	524
$1\ S - 4\ P$....................	196,100	510

Spectroscopic measurements have not as yet shown the presence of this series. Fricke and Lyman[26] observed only the single line at λ 585. This apparently has the notation $1\ S - 2\ S$, for the computed value, corresponding to the resonance potential 21.1 volts, is exactly this wavelength. The excitation of $1\ S - 2\ S$ is contrary to the Bohr principle of selection, but the line was emitted in a strong spark where, on account of the presence of the electrostatic field, the selection principle is not applicable. The line would not be absorbed by the surrounding *unexcited* gas, as for this the selection principle would hold. Lines of the series $1\ S - mP$, on the other hand, should show very great absorption. This probably explains why Fricke and Lyman could detect in their experiments the emission of only the line $1\ S - 2\ S$. If one could devise a continuous source of ultra-violet radiation in this extreme spectral range, it might be possible to obtain the series $1\ S - mP$ as absorption lines, analogous to Wood's work with sodium, page 80. Possibly "exploded wires"[27] could be employed to advantage in this respect.

[26] Phil. Mag., 41, p. 814 (1921). See footnote 39, page 77.
[27] Anderson, Astrophys. J., 51, pp. 37–48 (1920).

Using the photo-electric method described on page 137 Franck and Knipping[28] have obtained in helium at very low pressure some evidence for the presence of the lines $1\,S - 2\,P$ and $1\,S - 3\,P$. Their results expressed in volts are as follows:

Notation	Volts computed	Volts observed
$1\,S - 2\,P$	21.85	21.9
$1\,S - 3\,P$	23.7	23.6

The method is not conclusive, but merely suggestive.

If electrons are ejected to the $2\,s$ or $2\,S$ orbits of the helium atoms by low voltage electronic bombardment, it would appear that they should have difficulty in returning to the normal state. The return to $1\,S$ from $2\,s$ is prevented by the general law that intercombination lines between the crossed and coplanar orbital systems do not take place. The return from $2\,S$ is contrary to the selection principle and should therefore require the presence of a disturbing field. Hence the $2\,s$ and $2\,S$ states should represent metastable forms of helium, at least capable of existing for an appreciable length of time which is much greater than the life of the $2\,P$ state, for example.[29] This is evidenced by experimental work on the absorption of helium excited by a mild electric discharge. Paschen[30] observed that the gas very readily absorbed the lines $2\,S - 2\,P$, $\lambda = 20582$ and $2\,s - 2\,p$, $\lambda = 10830$. These lines were also reëmitted as resonance radiation (see page 86). From the fact that the scattered or resonance radiation for $2\,s - 2\,p$ was probably greater than that for $2\,S - 2\,P$, Franck and Reiche concluded that only the state $2\,s$ should be considered as a metastable modification of helium. In the $2\,s$ state with one electron revolving about the other in a

[28] Loc. cit.

[29] Since the above was written a paper more directly bearing on this point has been published by Kannenstine, Astrophys. J., 55, p. 345 (1922). A two-electrode Wehnelt arc in helium was excited by an alternating potential and the current-voltage characteristics were observed by use of a Braun-tube oscillograph. Operations were so controlled that after the arc had struck at a potential above the normal ionization point, it could be maintained at voltages as low as 4.8 volts. This voltage corresponds to the wave number $2s$ and accordingly represents the ionization potential of the helium atom in its $2s$ state. Now with a 60 cycle, applied potential, the arc was extinguished with each cycle, and was struck again only when the potential was greater than 25 volts. However, when the frequency of the applied potential was increased to between 200 and 220 cycles, the arc both struck and broke at 4.8 volts. This is interpreted to mean that the average life of the metastable helium atom in the $2s$ state is about one-half of the cycle, or of the order 0.002 seconds. As will appear in the section on "The Measurement of τ," Chap. IV, the time during which an outer orbit, not constituting a metastable configuration, may be occupied, is very much smaller, of the order 10^{-8} sec.

[30] Ann. Physik, 45, pp. 625–56 (1914).

coplanar orbit, helium should resemble lithium and might therefore be expected to be capable of forming compounds. Franck and Reiche have suggested several means, some involving processes of this type, by which the electron once in the 2 *s* orbit can return to normal without emitting the monochromatic wave number 1 *S* − 2 *s*. At the present time, however, most of these hypotheses are highly speculative and admitting the above general conclusions, the transitions from either 2 *s* or 2 *S* to normal, in the absence of a strong field, are not satisfactorily explained.

Kemble[31] and more recently Van Vleck[32] have questioned the possibility of identifying the 1 *S* state with the crossed orbit system described, so that Bohr's new computations of such orbits will be awaited with the greatest interest.

The Hydrogen Molecule

Bohr[33] proposed a model of the hydrogen molecule consisting of two nuclei each of unit positive charge, with two electrons revolving in the same circular orbit, the plane of which is symmetrically located perpendicular to the line joining the nuclei. The dimensions are fixed by the electric forces and the condition that each electron has one unit of angular momentum. The total energy of such a configuration is readily found to be $-2.20\,Nhc$ ergs. Referring to Equation (3) or (17) the energy of two normal hydrogen atoms is $-2\,Nhc$ ergs. The difference in these two values accordingly should give the work necessary to dissociate a hydrogen molecule into neutral atoms. This amounts to $0.20\,Nhc$ ergs or 2.7 volts. Bohr shows that a configuration for the molecular positive ion, consisting of the two nuclei and a single electron revolving about the line between them, is unstable and hence the removal of one electron from the molecule may result in its dissociation and the production of a neutral atom and an ionized atom. The total energy for the latter state is $-1.00\,Nhc$ ergs. The work required to ionize the molecule in this manner is accordingly $(2.20-1.00)\,Nhc$, which is equivalent to 16.2 volts.

This configuration of the hydrogen molecule must be rejected for the following and other reasons.

(1) Such a molecule would be paramagnetic, while hydrogen is known to be diamagnetic.

[31] Phil. Mag., 42, p. 123 (1921).
[32] Phys. R., 19, pp. 419–20 (1922).
[33] Phil. Mag., 26, pp. 857–75, (1913).

(2) Langmuir's[34] experimental determination of the heat of dissociation is 84000 cal/mol or 3.6 volts per molecule.[35]

(3) Positive ray analysis shows the existence of positive molecular ions.

The Bohr-Sommerfeld theory of the structure of the hydrogen *atom*, on the other hand, is satisfactory, as the many remarkable experimental confirmations of the series spectra and fine structure testify. As illustrated by Figure 4, the ionization potential of the atom should be 13.54 volts and the resonance potential 10.16 volts, corresponding to the convergence frequency and first line respectively of the Lyman series.

Measurements of the critical potentials for hydrogen by different observers show wide divergence both in the experimental values and in their interpretation. The results of Horton and Davies and of the authors, given in Table XV, are somewhat more consistent, showing two resonance potentials at 10.5 and 12 to 13 volts, a trace of ionization at a slightly higher point and strong ionization at 16 to 17 volts. Our values would immediately suggest the following interpretation, on the basis of Bohr's theory.

Volts Observed	Type of Collision		Volts Computed
	Observed	Theoretical	
10.4	Strong resonance	Atom: 1st line of Lyman Series	10.2
12.0	Faint resonance	Atom: 2d line of Lyman Series	12.0
13.3	Very faint ionization	Convergence of Lyman Series	13.5
16.0	Strong ionization	Molecule: Bohr's configuration	16.2

In spite of this apparent agreement between theory and experiment it is doubtful that the above table represents the correct analysis of the data, the difficulty being in the accounting for the presence of the quantity of monatomic hydrogen necessary to give such a pronounced indication of a resonance potential at 10.4 volts. In experiments where a hot cathode is employed there will be only a slight amount of thermal dissociation even for a wire operated at 2500° C. There is possibly

[34] J. Am. Chem. Soc., 34, p. 860 (1912).

[35] *Relation between volts per molecule and calories per gram mol.* The kinetic energy in ergs of an electron which has fallen through a field of x volts is given by Equation (66):

$$\text{ergs} = 1.592 \times 10^{-12}\, x \text{ volts} \quad (66)$$
$$\text{one } 20^\circ \text{ calorie} = 4.183 \cdot 10^{7} \text{ ergs} \quad (67)$$
$$\text{number of molecules per gram mol} = 6.06 \cdot 10^{23} \quad (68)$$
$$\text{Hence cal./mol} = 23070\, x \text{ volts/molecule} \quad (69)$$
$$\text{and kg cal./mol} = 23.07\, x \text{ volts/molecule} \quad (70)$$

sufficient dissociation, however, to account for the weak ionization observed at 13.3 volts. Using pressures of about 0.1 to 0.2 mm Hg in a discharge tube where the collisions occur over a space of 1 cm, it is found that about half of the electrons lose 10.4 volts velocity at this resonance potential. Now if $\frac{1}{2}\%$ of the gas at any instant had been dissociated by the hot wire, a very liberal estimate, only one collision in one hundred would have taken place with an atom. Hence one would conclude that half of the electrons collided some 100 times elastically in this small distance before encountering an atom responsible for the energy loss of 10.4 volts, a conclusion at variance with probability considerations. Thus it appears likely that the observed resonance potential of 10.4 volts, as well as 12.0 volts, is due to the molecule.

We have made experiments using a potassium hydride and potassium surface as a photo-electric source of electrons,[36] instead of a hot cathode. Precisely the same results were obtained, with the exception of ionization at 13.3 volts, in regard to which no conclusion could be drawn, as the sensitivity was not sufficient to detect this critical potential. It is doubtful whether monatomic hydrogen could have been present in such an apparatus, operated cold.

The possibility of dissociation by electron impact below the resonance potential is still an open question, but even so, this could scarcely account for a sufficient amount of atomic hydrogen to explain our results.

The agreement between the observed value of 16.0 volts for the ionization of the molecule and that predicted by Bohr's theory again must be of no significance. If ionization of the molecule results in a neutral atom and an ionized atom, the ionization potential should be $13.5 + 3.6 = 17.1$ volts, on the basis of Langmuir's determination of the work of dissociation. This disagreement with experiment suggests the possibility that a molecular ion is formed at this low voltage. In support of such argument we have found that the secondary spectrum of hydrogen predominates over the Balmer series below 20 volts, and the secondary spectrum is usually ascribed to vibrations of the molecule or molecular ion.

It is possible that the ionization potential of the molecule represents the work of dissociation plus the work of ionization of one atom minus the electron affinity E of the hydrogen molecule. We then obtain $13.5 + 3.6 - E_{\mathrm{H}} = 16.0$ or $E_{\mathrm{H}} = 1.1$ volts. Bohr's theoretical computation, based on the configuration which we have shown to be

[36] Mohler, Foote, and Kurth, Phys. R., 19, p. 414 (1922).

objectionable, gives 1.6 volts.[37] Further discussion of the question of electron affinity and dissociation is given in Chapter VIII.

Although we have questioned the ascribing of the 10.4 volt resonance potential, observed by the ordinary methods, to monatomic hydrogen for the reason that we cannot account for a sufficient quantity of the monatomic gas, there has never been any doubt as to the existence of a resonance potential corresponding to $\nu = N\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$ for the atom and an ionization potential corresponding to $\nu = N$, viz. 10.2 volts and 13.5 volts respectively. The well-known series relations require such critical potentials. Duffenback[38] has recently assured the presence of an atmosphere of monatomic hydrogen by operating the ionization chamber in a tungsten tube furnace at 2000 to 2500° abs. At 2500° abs and 1 mm pressure 98.8 per cent of the gas is dissociated into atoms. He found that with the furnace operated cold most of the ionization occurred at about 16 volts, but at the higher temperatures the current showed marked ionization at 10.3 and 13.2 volts. As will be discussed in Chapter VI, arcs may be struck at the lowest resonance potential, so that the appearance of the critical potentials 10.3 and 13.2 volts at high temperature where considerable dissociation occurs is a confirmation of the facts to be predicted from the line spectrum of the atom.

General References

Hughes, A. L., Bull. Natl. Res. Coun., 2, pp. 127–169 (1921). An excellent tabular summary of the experimental determinations of critical potentials to about March, 1921. As practically all observations by numerous observers are listed, many of which were not made under satisfactory experimental conditions, some judgment must be employed in selecting the most probable value where the range is wide.

McLennan, J. C., Phys. Soc., London, 31, pp. 1–29, 1918.

Franck, J., Physik. Z., 22, pp. 388, 409, 441, 466, 1921.

Gerlach, W., Vieweg's "Tagesfragen" Number 58, pp. 8–52 (1921). This contains a bibiliography of one hundred and thirty-three references. A large number of American and English papers published after 1916 are omitted, however, on account of their inaccessibility at that time.

[37] Bohr, Phil. Mag., 26, p. 863 (1913), shows that the total energy of the neutral hydrogen molecule on the above described configuration is $W = -2.20Nhc$ ergs. The total energy for the same configuration with three electrons instead of two in the common orbit, the plane of which is perpendicular to the line joining the nuclei, is shown to be $W' = -2.32Nhc$ ergs. Hence an amount of work $(2.32 - 2.20)Nhc = 0.12Nhc$ ergs *must be done on* the second system to reduce the molecular ion to the normal state. This is equivalent to 1.6 volts, a value which accordingly represents the electron affinity of the normal molecule.

[38] Science 55, pp. 210–211 (1922).

[39] Lyman, Science, 56, p. 167 (1922), finds in helium the following lines: λ 584.4, λ 537.1, λ 522.3, λ 515.7, and possibly λ 600.5. His paper appeared after this book was in page proof, too late to incorporate in the discussion on page 72. The first four lines are members of a series $1X - mP$ where $1X = 198290$ and $1X - 2S \approx$ fifth line above (approximately) $\approx$ first resonance potential. These observations conflict with measurements on ionization potential.

Chapter IV

Line Absorption Spectra of Atoms

Line Absorption Spectra of Normal Atoms

In accordance with the classical theories of radiation, as expressed by the usual interpretation of Kirchhoff's law, we should expect all emission lines of an element to appear as absorption lines[1] when a column of the vapor or gas is viewed against a source which emits a continuous spectrum. Experimentally, however, in any particular arrangement of apparatus we find that only for certain types of lines is absorption readily observed. The quantum theory of spectra satisfactorily accounts for this fact.

As a particular example we shall consider first the alkali metals. For the normal unexcited atom the valence or outer electron lies in the 1 *s* orbit. The atom accordingly is capable of absorbing monochromatic radiation in quanta of a frequency or energy value just sufficient to displace the valence electron to an outer orbit. Radiation of frequency corresponding to energy *intermediate*[2] to two outer orbits leaves the atom unaffected. The atom is unable to resonate to such frequencies; it cannot absorb them because there is no position of equilibrium which the atom could assume and retain the energy. It cannot absorb a portion of the energy just sufficient to reach a stable configuration because the incident radiation exists in discrete indivisible quanta which must be absorbed in toto or not at all.

By the Bohr principle of selection the azimuthal quantum number in any interorbital transition of an electron must change by $\pm$ 1 unit. Hence only those frequencies of the incident radiation will be absorbed which result in the ejection of the valence electron to orbits for which the azimuthal quantum number differs by unity from the normal state. This requires that the electron pass from the 1 *s* orbit to an *mp* orbit where *m* may have any value from 2 to ∞. Hence only radiation of

[1] With some exceptions of academic interest.
[2] For other cases, see Chapter X.

wave number $\nu = 1\ s - mp$ is absorbed from the continuous source. The long column of absorbing vapor thus accumulates energy and would continue to increase in energy until the valence electron of every atom finds itself in a *p*-orbit, *but for the following two facts:* (1) An atom having its electron in a *p*-orbit or any other outer orbit is described as an "excited atom" and is capable of absorbing other characteristic radiation. This interesting phase of absorption spectra is treated in a following separate section. (2) The electron once displaced almost instantly resumes its normal 1 *s* position.

If the electron displaced to the *mp* orbit returns to the 1 *s* orbit in a single jump, the line $\nu = 1\,s - mp$ is emitted. This emission, however, for the long column of gas is spread over a solid angle $4\,\pi$, whereas the radiation absorbed from the source is confined to the narrow beam passing through the gas. Radiation of frequency $\nu = 1\,s - mp$ is accordingly abstracted from the beam of small solid angle and subsequently, by the above described indirect process, scattered in all directions. The result is that along the line of sight far more radiation is absorbed than is emitted and the lines $\nu = 1\,s - mp$ stand out as sharp absorption lines against the continuous source and the scattered radiation.

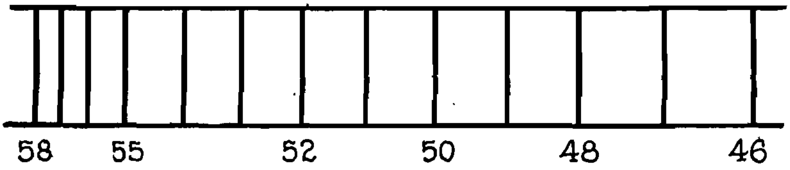


FIG. 12. Principal series lines of sodium from $m = 46$ to 58, observed as absorption lines.

In general if 1 *s* or 1 *S* represents the normal orbit of the electron in the unexcited atom, we should expect to observe as absorption lines the wave numbers $\nu = 1\ s - mp$ for the alkalis; $1\ S - mp_2$ and $1\ S - mP$ for the metals of Group II of the periodic table and similarly for the other groups. Lines in emission series which converge at 1 *s* or 1 *S*, when the orbits corresponding to these frequencies represent the normal state, should be absorption lines, characteristic of the normal atom.

The experimental verifications of this simple theory are conclusive. Wood and Fortrat,[3] using in effect a train of thirteen 60° quartz prisms, have examined the absorption spectra of a long column (3 meters: 20 meters recommended) of sodium vapor of fairly low den-

[3] Wood and Fortrat, Astrophys. J., 43, pp. 73–80 (1916).

sity. The only absorption lines appearing belonged to the principal series $1\,s - mp$. These were observed to $m = 58$, fifty-seven pairs, although the resolution was not sufficient to separate the pairs beyond $m = 8$. The last thirteen observed members of the series are indicated, on a wave-length scale, by Figure 12. The wave-length corresponding to the convergence frequency lies to the left of the line $m = 58$ about the distance equal to the length of the portion of the series illustrated. On this scale the D-lines would lie to the right a distance of 1100 feet. Line $m = 46$ differs in wave-length from line $m = 58$ by about one Angstrom unit.

Figure 13 illustrates the line absorption spectrum of sodium. The upper spectrogram is from a negative made by Dr. G. R. Harrison and shows the absorption of the second, third and fourth members of the principal series. At low vapor pressure these lines are very sharp. If the pressure is increased, higher terms are brought out, but the absorption of the first members widens into broad bands, as shown by the lower spectrogram made by Prof. Wood. The central spectrogram, also Wood's, shows the line absorption clearly, nearly to the head of the series. We have marked twenty-one terms, but many more were readily visible in the negative. The emission lines in these illustrations are due to the cadmium or aluminum spark in air employed as a source.

The exact physical significance of the broadening of the lines at high pressure has not been satisfactorily interpreted by the quantum theory.[4] The necessity for employing high pressure in order to bring out higher terms is to be expected. The chance that an electron be displaced to say the 58th orbit is small when there are so many orbits of nearly identical energy value. By increasing the pressure the number of atoms is increased with a proportionate change in the probability of a displacement to any individual orbit, and the resulting absorption of the corresponding line. The same effect might be produced by increasing the length of the column of vapor. The phenomenon at high pressure is, however, complicated possibly by the interpenetration, or certainly by the perturbations, of orbits of electrons in neighboring atoms.

Wood's work on sodium has been extended to the other alkali vapors by Bevan.[5] In this manner terms of the principal series were obtained as absorption lines to $m = 25$ for potassium, $m = 26$ for rubidium, $m = 22$ for caesium and $m = 28$ for lithium.

[4] See page 91.
[5] Proc. Roy. Soc. Lond., 83, pp. 421–28 (1910); 85, pp. 54–8 (1910).

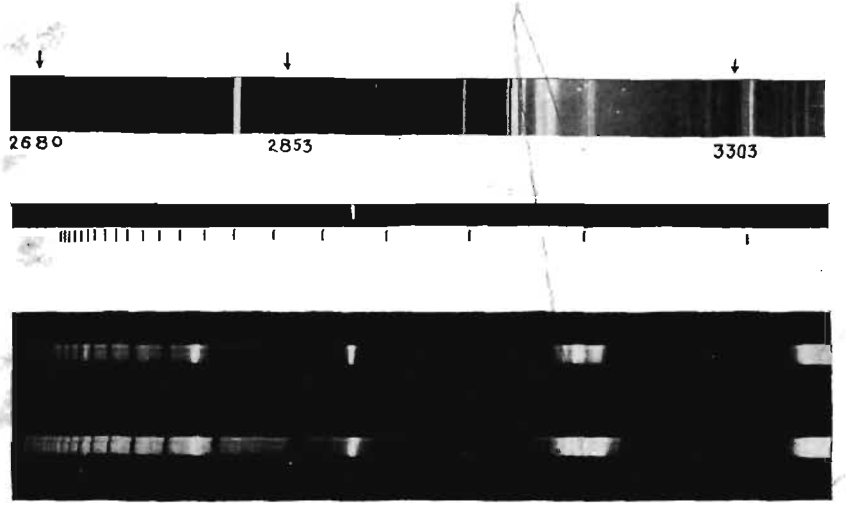


FIG. 13. Absorption spectrum of sodium, showing absorption of principal series lines. The bright lines are due to the source of light.

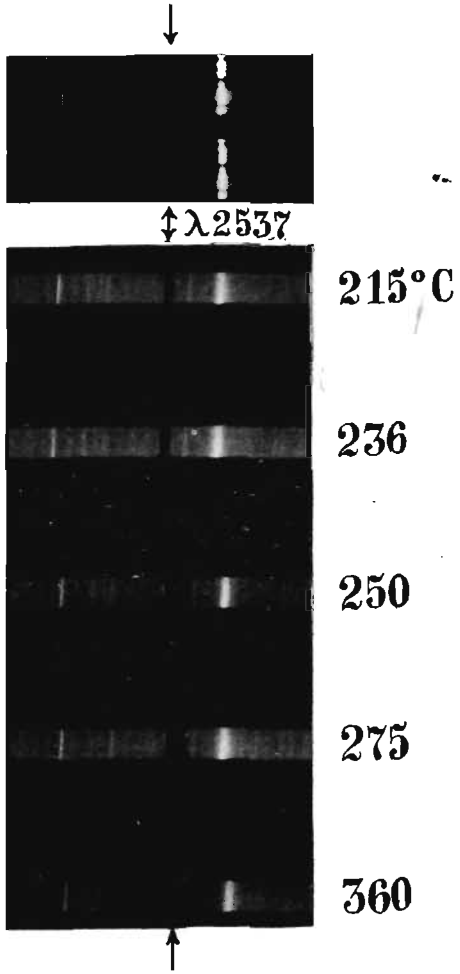


FIG. 14. Absorption spectrum of mercury showing the absorption line λ 2537, $1S - 2p_2$. The emission lines are due to the source of light.

COLLEGE AND
10 JUN 1924

FIG. 14A. Absorption of mercury λ 2537. The continuous spectrum is produced by an aluminum spark under water. Tungsten electrodes are still better.

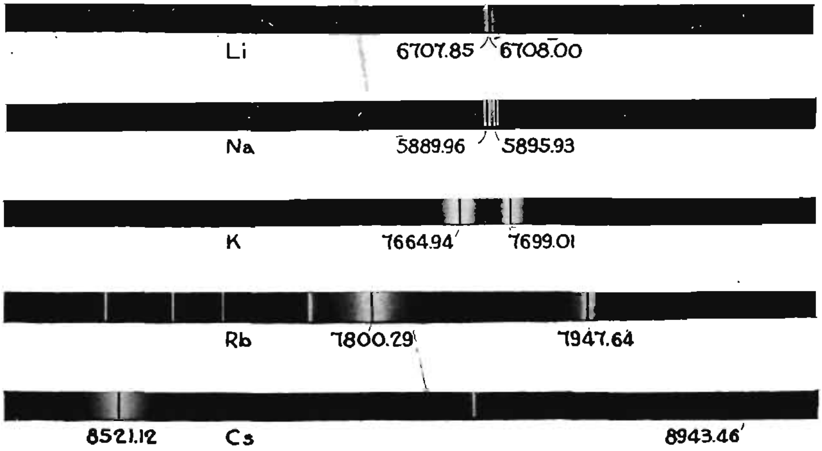


FIG. 15. Reversals of the first pair of the principal series for the alkalis. The illustrations have been prepared on the same scale of wave-lengths.

FIG. 15A. Illustrating the practically complete absorption of rare mercury vapor f
the resonance radiation λ 2537.

AGRICULTURAL COLLEGE AND ... INSTITUTE LIBRARY
10 JUN 1924

The important series converging at 1 S for the metals of Group II are mainly confined to the ultra-violet. Wood first showed that the mercury line 1 $S - 2\ p_2$, $\lambda = 2537$, is strongly absorbed by a column of mercury vapor. Figure 14, by Wood, illustrates this absorption very clearly. At low pressure, the absorption is very sharply defined, but as the pressure of the vapor is increased, by increasing the temperature as indicated, the line widens into a band. The absorption of this line is now a matter of common experience in the operation of a quartz mercury vapor lamp. If the lamp is overheated. as was first pointed out by Wood, its actinic effect is greatly reduced on account of the absorption of λ 2537 by the dense vapor. A photograph of the arc under such conditions shows almost complete absence of this line. On account of the continuous spectrum which is produced with strong current and high temperature λ 2537 may appear as a strong reversal against the faint background of the continuous emission spectrum.

Wood and Guthrie[6] found absorption in cadmium vapor for the lines 1 $S - 2\ p_2$, λ 3260 and 1 $S - 2\ P$, λ 2288. McLennan and Edwards[7] have demonstrated that the mercury line 1 $S - 2\ P$, λ 1849, is entirely absorbed by a column of rare mercury vapor, but did not succeed in obtaining it as a reversal against a continuous background. The experimental difficulty here is in producing a suitable continuous source of ultra-violet light. The best method so far devised[8] is the use of an aluminum or preferably tungsten spark gap immersed in water and excited by a very high voltage, using a Tesla coil, auxiliary air gap and capacity. This gives a continuous spectrum throughout the visible and in the ultra-violet at least to the limit of the quartz spectrograph. It is obviously not suitable however for work with the vacuum spectrograph. For this range the Lewis[9] method employing hydrogen offers a little hope, but its use is necessarily restricted. One will readily appreciate the almost insurmountable difficulties in the determination of absorption spectra of metallic vapors below λ 2000.

McLennan and Edwards besides corroborating Wood's work observed absorption and complete reversal against a brighter background,

[6] Astrophys. J., 29, p. 211 (1909).

[7] *Phil. Mag.*, 30, pp. 695–700 (1915).

[8] The electrical arrangement is described by Howe, Phys. R., 8, p. 681 (1916). Fig. 14A shows the beautiful continuous spectrum which is easily obtained. If only the central portion of the spark is employed practically no trace of emission lines is present. In this spectrogram Dr. Meggers and the authors were endeavoring to obtain the line absorption spectrum of arsenic vapor. This was unsuccessful, but the absorption of the mercury line λ 2537 is very pronounced, arising in the mercury which was present with the arsenic vapor. The mercury emission spectrum is also shown for comparison. More recent descriptions of the spark apparatus are given in "Transmissivity of Food Dyes." Bur. Standards Sci. Paper No. 440.

[9] Science, 41, p. 947 (1915); Phys. R., 16, p. 367 (1920). Hulburt, Astrophys. J., 42, p. 205 (1915).

in rare zinc vapor, of the zinc line $1\ S - 2\ p_2$, λ 3076 and complete absorption of $1\ S - 2\ P$, λ 2139.

McLennan[10] using a column of magnesium vapor obtained reversal of the line $1\ S - 2\ P$, λ 2852, and showed the presence of absorption for $1\ S - 3\ P$, λ 2026. For some unexplained reason he could not detect absorption of the fundamental line $1\ S - 2\ p_2$, λ 4571.

King's[11] work on furnace spectra shows that fundamentally important lines are readily absorbed and may appear as reversals against the brighter background of the furnace walls, for example λ 4227, $1\ S - 2\ P$, of calcium. King states that in general, for all metals the strong absorption lines are those which are excited as emission lines at low temperature. Among these latter, as will appear in Chapter VII, are to be found the fundamental lines of series converging at 1 *S* or 1 *s*, at least insofar as the spectral region investigated covers that embraced by these series.

Reversed Lines

The spectrum of a material obtained in an ordinary arc is in general composed of emission lines. However, under certain conditions lines are reversed, appearing black against the brighter background. An example of this is shown by Figure 15, prepared by Meggers, for the first pair in the principal series of each of the alkalis. The reversed portion, which appears black, is much narrower than the emission line, showing in the reproduction as a white band.[12] Generally absorption lines are more nearly monochromatic than the corresponding emission line, in part because of the smaller Doppler effect and lesser pressure of the cooler vapor, but also for other reasons which have not been satisfactorily explained. The reversal is due to absorption of the emitted light by the zone of cooler vapor surrounding the arc. In the illustration given the emission line for caesium is exceptionally broad. Frequently, however, the emission lines are narrow and the reversal may then almost or even completely cover the emission. Reversals are found even in flame spectra. A narrow reversal of the D-lines against the broader background of the emission spectrum is readily observed in a long train of bunsen burners fed with salt.

Probably reversals in the arc can be obtained for all lines of series converging at 1 *s* or 1 *S*. The observation of a reversal, however, does not indicate that the line belongs to these series. Among the thousands

[10] McLennan, Proc. Roy. Soc., 95, pp. 273–9 (1919).
[11] Astrophys. J., 51, pp. 13–22 (1920).
[12] It is of interest that the square root of the doublet separations for the alkalis $\sqrt{\Delta\nu}$ plotted against atomic number gives an approximately straight line.

of reversals listed in the spectroscopic tables will be found all types of lines, including those belonging to subordinate and combination series, series converging at 2 s, etc., the explanation of which is given in the section on excited atoms and in Chapters VI and VII. On the other hand by careful consideration of reversed lines considerable information may be derived concerning series relations. Thus with copper we find a strong reversal of the pair λ 3248 and λ 3275, which fact combined with our somewhat unsatisfactory knowledge of the series relations for this element enables us to predict with a fair degree of certainty that this is the pair $1\,s - 2\,p$ which determines the value of the resonance potential. For the same reason we are led to suspect that λ 2428 is a member of the principal series of gold, and is likely the term $1\,s - 2\,p_1$, although the series relations are entirely unknown. The fact that all the lines of Paschen's principal series of thallium are so readily reversed in the arc is a strong argument for assigning the notation 1 s to the convergence frequency instead of 2 s, as suggested in the chapter on ionization potential. In this particular case, however, the vapor may be "excited" by the high temperature, as discussed in Chapter VII. Under such conditions the fundamentally important lines should be suppressed both in emission and absorption, especially so since the resonance potential is extremely low. The work of Wood and Guthrie[13] on absorption of thallium vapor is suggestive but inconclusive and should be repeated using as long a column of vapor at as low a temperature as practicable.

McLennan and Young[14] have made an investigation of the arc reversals for calcium, strontium and barium. They observed the first six lines of the series $1\,S - mP$ as reversals in calcium, ten lines of this series in strontium and nine lines in barium.[15]

One finds in the spectroscopic tables that at least the first term of the series $1\,S - 2\,P$ and $1\,S - 2\,p_2$ has been observed reversed for most of the elements of Group II. In Table XVI are listed several of the early members of these series. A few of these lines are merely computed values, having been unobserved as yet either in emission or absorption. In the last column, A denotes that the line has been observed as an absorption line, using a long column of vapor; R as a reversal in an arc; K as a reversal in furnace spectra, and F as an emission line in flame spectra. It is noted that the wave-lengths of many of the lines are less than 2000 A. These accordingly can be best studied, for absorption,

[13] Astrophys. J., 29, p. 211 (1909). [14] Proc. Roy. Soc. 95, pp. 273–9 (1919).
[15] Two of these were assigned entirely incorrect wave-lengths, viz., $1S - 3P$ and $1S - 4P$ for barium.

as reversals in arcs. A suggested method suitable for the vacuum spectograph is to employ a very long vertical tube with a Wehnelt cathode arc at the bottom. The metal is boiled at the bottom and condensed in the upper part of the tube, at the top of which is mounted the spectrograph, sufficiently distant to prevent contamination. The emission lines will be broad on account of the higher pressure at the bottom of the tube, thus furnishing a background for the absorption lines produced by the long column of rarer vapor. There is, however, still a splendid field for work at wave-lengths longer than 2000 A. especially with elements of other groups of the periodic table.

TABLE XVI

IMPORTANT (FROM STANDPOINT OF ATOMIC STRUCTURE) SERIES LINES FOR METALS OF GROUP II. COMPILED BY F. A. SAUNDERS

Element	Notation	ν	λ (*vacuum*)	λ (*air*)	Remarks[16]
Mg.	$1S$	61672	1622		
	$1S-2p_2$	21871	4572	4571	F K
	$1S-3p_2$	47853	2090		
	$1S-4p_2$	54253	1843		
	$1S-5p_2$	57020	1754		
	$1S-2P$	35051	2853	2852	AFR K
	$1S-3P$	49347	2026		R K
	$1S-4P$	54703	1828		
Ca.	$1S$	49305	2028		
	$1S-2p_2$	15210	6575	6573	K
	$1S-3p_2$	36555	2736	2735	
	$1S-4p_2$	42519	2352		
	$1S-5p_2$	44962	2224		
	$1S-2P$	23652	4228	4227	R K F
	$1S-3P$	36732	2723	2722	K
	$1S-4P$	41679	2399	2399	RK
	$1S-5P$	43933	2276	2275	RK
Zn.	$1S$	75767	1318		
	$1S-2p_2$	32502	3077	3076	ARF K
	$1S-3p_2$	61274	1632		
	$1S-4p_2$	68081	1469		
	$1S-5p_2$	70982	1409		
	$1S-2P$	46745	2139	2139	AR K
	$1S-3P$	62902	1590		
	$1S-4P$	68608	1458		
	$1S-5P$	71215	1404		

[16] A denotes that the line has been observed as an absorption line using a long column of rare vapor. Continued on page 85.

TABLE XVI — *Continued*

IMPORTANT (FROM STANDPOINT OF ATOMIC STRUCTURE) SERIES LINES FOR METALS OF GROUP II. COMPILED BY F. A. SAUNDERS

Element	Notation	ν	λ (*vacuum*)	λ (*air*)	Remarks[16]
Sr	$1S$	45926	2177		
	$1S-2p_2$	14504	6895	6893	K
	$1S-3p_2$	33869	2953	2952	
	$1S-4p_2$	39426	2536		
	$1S-2P$	21698	4609	4607	RF K
	$1S-3P$	34098	2933	2932	K
	$1S-4P$	38907	2570	2570	RK
	$1S-5P$	41172	2429	2428	RK
Cd	$1S$	72539	1379		
	$1S-2p_2$	30656	3262	3261	ARFK
	$1S-3p_2$	58462	1711		
	$1S-4p_2$	65027	1538		
	$1S-5p_2$	67842	1474		
	$1S-2P$	43692	2289	2288	ARFK
	$1S-3P$	59906	1669		
	$1S-4P$	65494	1527		
	$1S-5P$	68056	1469		
Ba	$1S$	42029	2379		
	$1S-2p_2$	12637	7913	7911	K
	$1S-3p_2$	30815	3245	3244	K
	$1S-4p_2$	35892	2786		
	$1S-2P$	18060	5537	5535	RFK
	$1S-3P$	32547	3072	3072	RK
	$1S-4P$	36990	2703	2703	RK
	$1S-5P$	38500	2597	2597	RK
Hg	$1S$	84178	1188		
	$1S-2p_2$	39413	2537	2537	ARFK
	$1S-3p_2$	69656	1436		
	$1S-4p_2$	76464	1308		
	$1S-5p_2$	79410	1259		
	$1S-2P$	54066	1850		AK
	$1S-3P$	71291	1403		
	$1S-4P$	78810	1269		
	$1S-5P$	79961	1251		

[16] (*Continued*) R denotes that the line has been observed as a reversal in an arc.
K denotes that the line has been observed as an absorption line in furnace spectra, *i.e.*, reversed against the bright walls of the furnace.
F denotes that the line has been observed as an emission line in a flame.
For relation between λ (*vac*) and λ (*air*) see data of Meggers and Peters, Smithsonian Tables, 7th Ed., p. 293. Also Bul. Bur. Standards, 14, p. 731 (1918).

Resonance Radiation

As stated earlier, the mechanism of line absorption of vapors involves the re-emission of the radiant energy absorbed. This re-emitted light, called resonance radiation, has been studied in considerable detail for sodium and mercury.[17] If a bulb of pure sodium vapor at low pressure is illuminated by a beam of light from a sodium flame or vacuum arc, the vapor will diffusely emit radiation consisting of only the two D-lines, $1\ s - 2\ p_1$ and $1\ s - 2\ p_2$. At very low pressure, less than that corresponding to saturation at 150° C, the entire bulb is filled with a faint glow. As the pressure is increased the diffusely emitted light becomes concentrated near the place of incidence of the exciting beam of radiation, and at 250° C, pressure about 0.01 mm, is confined to the extreme surface.

These phenomena show that the effective part of the incident radiation is absorbed in a very thin layer of the vapor at the higher temperature while at lower temperatures and pressures the radiation penetrates the bulb and is passed on from atom to atom throughout the volume.

Analysis of the emitted light by the interferometer shows that the entire width of the lines, about 0.03 A, may be accounted for by the Doppler effect alone of the vapor at this comparatively low temperature. Only a portion of the exciting D-radiation is absorbed so that the beam passing through the vapor shows a very narrow absorption line in the center of each of the broad, transmitted D-lines.

Strutt[18] has found that the sodium doublet $1\ s - 3\ p$, λ 3303, likewise excites resonance light. In this case the emitted radiation consists of *both* D-lines and radiation of the frequency absorbed, λ 3303. This is in accord with the quantum theory. Absorption of a quantum of radiation of wave-length λ 3303 ejects an electron from the $1\ s$ orbit to either the $3\ p_1$ or $3\ p_2$ orbit. This energy may be given up either by a direct return to $1\ s$ with the emission of $1\ s - 3\ p$ or indirectly by a transition to $2\ p$ and from there to $1\ s$, the latter step involving the emission of the D-lines. The Bohr principle of selection shows that, in the absence of a disturbing field, a direct fall from $3\ p$ to $2\ p$ with the emission of $2\ p - 3\ p$ should not occur, a fact confirmed by Strutt. The transition between these two orbits must be made through either the $2\ s$ or $3\ d$ orbit as an intermediate stage, as shown by Figure 9. The following table illustrates the various steps involved as a consequence

[17] Cf. Wood's "Physical Optics," 2d Ed. The discovery and a great part of the development of this subject is due to Wood and his co-workers.
[18] Proc. Roy. Soc., 96, pp. 272–86 (1919).

of the absorption of $1\,s - 3\,p_1$. A similar table may be prepared for an initial absorption of $1\,s - 3\,p_2$ in which all steps from **d** on are the same as here given. Absorption of $1\,s - 3\,p_1$ accordingly may be followed by emission through the successive stages **b** or **c**, **e**, **i**, or **d**, **g**, **i** or **d**, **h**, **j**, etc. With many atoms returning to normal by different paths, all of the lines given in this table may be emitted. Strutt's observation that both D-lines as well as $1\,s - 3\,p$ are emitted when the exciting radiation is $1\,s - 3\,p$ is accordingly confirmed by the theory. The reason that Strutt did not observe the other lines listed is because they all lie in the infra-red.

TABLE XVII

Step	Position of Valence Electron		Radiation		Wave-length in A
	Initial	Final	Notation	Remarks	
a	$1\,s$	$3\,p_1$	$1\,s - 3\,p_1$	absorbed	3302.5
b	$3\,p_1$	$1\,s$	$1\,s - 3\,p_1$	radiated	3302.5
c	$3\,p_1$	$3\,d$	$3\,d - 3\,p_1$	"	90480.
d	$3\,p_1$	$2\,s$	$2\,s - 3\,p_1$	"	22056.9
e	$3\,d$	$2\,p_1$	$2\,p_1 - 3\,d$	"	8196.1
f	$3\,d$	$2\,p_2$	$2\,p_2 - 3\,d$	"	8184.5
g	$2\,s$	$2\,p_1$	$2\,p_1 - 2\,s$	"	11404.2
h	$2\,s$	$2\,p_2$	$2\,p_2 - 2\,s$	"	11382.4
i	$2\,p_1$	$1\,s$	$1\,s - 2\,p_1$	"	5890.2
j	$2\,p_2$	$1\,s$	$1\,s - 2\,p_2$	"	5896.2

If sodium vapor is excited by one of the D-lines alone, we should expect that only this line would appear in the resonance radiation, since a transition from $2\,p_1$ to $2\,p_2$ involving an emission of $2\,p_2 - 2\,p_1$ is contrary to the Bohr principle of selection and a transition from $2\,p_2$ to $2\,p_1$ requires additional energy. Wood and Dunoyer[19] concluded that resonance radiation excited by one D-line consisted of that D-line alone. Wood and Mohler,[20] however, later, showed that this was true only at extremely low pressure. If the pressure of the sodium vapor is increased or if hydrogen is added, both D-lines appear when the excitation is by either D_1 or D_2 alone. It is possible that the principle of selection is broken down at high pressure by the disturbing field of

[19] Phil. Mag., 27, p. 1018 (1914).
[20] Phys. R., 11, p. 70 (1918).

neighboring atoms. In such case by excitation with $1\ s - 2\ p_1$ the infra-red line $2\ p_2 - 2\ p_1$, $\lambda\ 590\ \mu$ (1/17 cm), may be emitted with the subsequent emission of $1\ s - 2\ p_2$. For the same reason excitation by $1\ s - 2\ p_2$ may be followed by absorption of $2\ p_2 - 2\ p_1$ from the continuous emission spectrum, black-body distribution, of the walls of the vessel or room. This would eject the electron to the $2\ p_1$ orbit, thus permitting the subsequent emission of $1\ s - 2\ p_1$. It is also possible, when we are concerned with such extremely minute quantities of energy as are represented by quanta of wave-length 1/17 cm, that atomic collisions may play an important rôle and that the transfer of the electron between $2\ p_1$ and $2\ p_2$ is the direct result of slightly inelastic collision. Under such circumstances the principle of selection would not be violated.

Mercury vapor at low pressure shows resonance radiation for the line $\lambda\ 2537$, $1\ S - 2\ p_2$. No investigation has been made with excitation by other fundamental lines, $1\ S - 3\ p_2$, $1\ S - 2\ P$, etc., since they lie in an inconvenient spectral region, as shown by Table XVI. If the width of the resonance line is due entirely to the Doppler effect, we have for the vapor at room temperature:

$$\text{width of line} = 0.86 \cdot 10^{-6}\lambda \sqrt{T/M} = 0.0026 \text{ Angstrom.}$$

Hence to observe the absorption of this line or the reversal of such a narrow line against the broad emission spectrum should require high resolving power. The pressure of mercury vapor at room temperature is about 0.001 mm Hg; at 60° C, 0.02 mm; at 100° C, 0.28 mm. This small variation in temperature does not materially change the Doppler effect, yet at even 60° C the absorption of a short column of mercury vapor may be readily observed with a prism spectrograph and a pronounced reversal obtained against a continuous source, similar to the reversals shown in Figure 14. It is an experimental fact that absorption of $\lambda\ 2537$ by mercury vapor at 20° C cannot be detected with an ordinary prism-spectrograph, because of the insufficient resolution. Yet a very short column of rare vapor is opaque to a portion of this line, a fact simply and clearly demonstrated by Wood. A saucer containing mercury at room temperature was photographed with a quartz-lens camera against the resonance radiation emitted by a bulb of mercury vapor, which was excited by a beam of radiation $\lambda\ 2537$. The photograph showed the opaque clouds of the vapor rising over the dish. If the photograph is made with an ordinary source of $\lambda\ 2537$, many times broader than the absorption line, the vapor above the saucer appears transparent.

Figure 15 A obtained by Wood[21] shows the shadow cast by a quartz bulb filled with mercury vapor at room temperature when illuminated by the mercury resonance radiation. The opacity of the extremely rare vapor to this radiation is readily apparent, the entire bulb appearing black.[22]

If a beam of λ 2537 from an ordinary mercury arc passes through a column of mercury vapor at low pressure the scattered light is not confined to the geometrical boundary of the beam, but as mentioned earlier for sodium, is diffusely radiated throughout the vapor. Wood[23] has measured the rate at which the intensity decreases in mercury vapor at 0.001 mm Hg pressure in a direction at right angles to the geometrical boundary of the beam as follows:

Distance	Relative Intensity
0.0 mm	1/1
0.5	1/3
1.5	1/6
2.5	1/10
3.5	1/30

These data probably give an approximate measure of the absorption coefficient of the vapor for the resonance radiation. For example, 0.5 mm of mercury vapor at 0.001 mm Hg pressure may reduce the intensity of a beam of resonance radiation to 1/3 its initial value. It is unfortunate that the value of the absorption constant, the importance of which will appear in Chapter VI, has not been measured by a more direct method, but very likely the experimental difficulties would be considerable.

An exact definition of resonance radiation is difficult to formulate. Originally the term referred to the radiation of the same wave-length as that of the exciting source, emitted by a vapor which before the excita-

[21] "Researches in Physical Optics," Part I, Columbia University Press.

[22] In a recent letter R. W. Wood gives the results, as yet unpublished, of experiments on the intensity of mercury resonance radiation. The intensity is increased by the addition of helium or argon, although other gases reduce the intensity of the radiation or destroy it entirely. In helium at 33 cm, the radiation is 4 times as strong as in Hg vapor alone at room temperature (.001 mm pressure). The complete explanation of these phenomena is probably quite complicated, but it has been shown experimentally that the increase of intensity by helium is due to the fact that the spectral range absorbed (out of the middle of the broad 2537 exciting line) is widened, so that more energy is diverted from the primary beam. This was proved by first passing the exciting beam of λ 2537 light through a cell of Hg vapor in vacuo. It was thus freed of all frequencies capable of exciting Hg vapor in vacuo; however, it excited powerfully Hg in helium.

[23] "Researches in Physical Optics," Part I, p. 54.

tion was in a normal state. Hence the D-lines stimulated by the D-lines may be called resonance radiation, while the excitation of the D-lines by the second pair of the principal series would not fall within this classification. We shall see, however, in the following section that an atom having an electron in an outer orbit, for example the 2 p_2 orbit, is capable of absorbing the first line of a subordinate series and subsequently may re-emit the line as strictly resonance radiation. Accordingly, even if we rigidly restrict the terminology resonance radiation to the emission of the same radiation as that of the stimulating source, any line whatever may be a resonance line depending upon the state of the vapor. If the atoms are in a normal condition, lines of the fundamentally important series converging at 1 S or 1 s may be resonance lines. If the atoms are "excited,"as explained in the following section, lines of other series may show resonance radiation. The phenomenon is simply a consequence of absorption. Any line which is absorbed, by a monatomic vapor, from a beam of radiation, subsequently *may be* radiated in all directions, and observed as scattered light.

It may be that the definition of resonance radiation should be restricted, as advocated by Franck, to the case where the emitted frequency is the only one possible. This would require in general that the first line of a principal series, converging at 1 S or 1 s, or a combination line if of lower frequency, should be a resonance line, for example 1 s − 2 p for the alkalis and 1 S − 2 p_2 for the alkali earths. Further, since transitions from 2 P to 2 p_2 in the absence of a disturbing field are contrary to the Bohr selection principle, the line $1S - 2P$ should be a resonance line for metals of Group II even upon the above restricted definition. Franck classes the scattered emission of the line 2 s − 2 p of helium, λ 10830, as resonance radiation because the 2 s state is a metastable configuration and an electron in the 2 p orbit can give rise to the emission of only 2 s − 2 p.

The phenomena of resonance radiation must not be confused with the fluorescence of metallic vapors. Fluorescent spectra are best observed with much greater vapor densities and with intense illumination. The emitted radiation is very complicated and depends upon the wave-length of the exciting source. The stimulus may have an entirely different wave-length from any line in the emission spectrum of the pure vapor. As briefly described in the latter part of this chapter, fluorescence may be generally ascribed to unstable, polyatomic, molecular formations.

THE BROADENING OF SPECTRAL LINES

We have seen that the narrow portion of the line λ 2537, represented by the resonance radiation from mercury vapor at room temperature, is almost totally absorbed by a very short column of mercury vapor at 0.001 mm pressure, while by increasing the pressure to several mm the entire line is absorbed. On further increase in pressure the line widens into a band.

The increase in width of an absorption, or emission, line has been considered from the classical dynamical standpoint by Rayleigh,[24] Lorentz[25] and others. Rayleigh discusses five different causes for broadening, and Franck[26] has interpreted three of these in relation to the quantum theory. Two causes, the Doppler Effect and Impact Damping, are of particular interest.

Doppler Effect. From the classical theory, a quasi-elastically bound electron, vibrating with a frequency $\bar{\nu}_0$ and moving with a velocity v in a direction making an angle ϕ with the line drawn from the atom to the observer gives rise to the frequency

$$\bar{\nu} = \bar{\nu}_0 \left(1 + \frac{v}{c} \cos \phi\right),$$

where c is the velocity of light. In consequence of the Maxwellian distribution of velocities of the atoms of a radiating gas, we have a broadening of the spectral line about the monochromatic frequency $\bar{\nu}_0$, which leads directly to the useful expression given on page 27 for the width of a line. In general v is small compared to c, so that the broadening amounts to only a few hundredths of an Angstrom. In the case of canal rays, however, we have a stream of radiating atoms projected with high velocity in a single direction, so that instead of a broadening we have a shift of frequency $\Delta\bar{\nu} = \mp \bar{\nu}_0 \frac{v}{c}$, according as one looks with or against the direction of propagation of the beam, amounting to an easily observable quantity, of the order of an Angstrom unit.

The above explanation, which is so simple from the classical dynamical standpoint, especially in its relation to familiar acoustical phenomena, is by no means satisfactory on the basis of the quantum theory. Here we give individuality to the quantum and are led to question how the energy of a quantum projected in the direction of the beam may differ

[24] Phil. Mag., 29, pp. 274–84 (1915).
[25] K. Akad. Amsterdam Proc., 18, pp. 134–50 (1915).
[26] "The Broadening of Spectral Lines," 5 pp., Anniversary Volume of Kais. Wilh. Ges. (1921).

by 2 $h\Delta\bar{\nu}$ ergs from that projected at 180° to this direction. The explanation lies in the effect of the radiation pressure. The emission of a quantum projected in the direction of the speeding atom produces a recoil upon the atom and retards it. The quantum thereby abstracts from the kinetic energy of the atom, $h\Delta\bar{\nu}$ ergs, so that the frequency of emission is increased by $\Delta\bar{\nu}$. If the emission takes place in a direction opposite to that along which the atom is projected, the atom is accelerated by the emission, its kinetic energy is increased by $h\Delta\bar{\nu}$ ergs, and the frequency of the quantum is lowered by $\Delta\bar{\nu}$.

The magnitude of the Doppler effect thus remains the same, but the interpretation of the phenomenon is different by the two theories.

Impact Damping. At high pressure and also in a strong electrical discharge the broadening of lines may be many times greater than that attributable to the Doppler effect. Lorentz considered this phenomenon as due to impacts from neighboring atoms which an atom suffers during the process of emission. If the emission is broken up by the impact, or if a phase change is produced, it may be shown that the emitted radiation will consist of a dispersion of frequencies which is greater the shorter the time of the undisturbed emission. Since the number of impacts increases with increasing pressure, we obtain an increase in broadening of the line, a fact well established by experiment.

The quantum theory substitutes for impact damping the influence of the electrical fields of neighboring atoms upon the position and energy of the electron in a quantized orbit. Since the energy of any orbit is altered, the energy difference of the two orbits between which an electron jump takes place may be changed, with a resulting modification of $h\bar{\nu}$.

As will appear in the following section, an electron may occupy an outer orbit in an undisturbed atom for an appreciable length of time τ. Franck believes that if such an atom which is in a condition to emit a spectral line, collides with another atom, the time τ is immediately altered and the emission is forced to take place while the orbits of the radiating atom are deformed by the electrical field of the impacting atom. Since all types of collision may occur, resulting in different degrees of orbital deformation, a dispersion of frequencies will be produced with a resulting broadening of the emission line. Also since the number of collisions increases as the pressure is raised, the amount of broadening should increase. An analogous interpretation may be given to the phenomenon of absorption so that probably the remarkable broadening of the absorption lines noted in the foregoing section is mainly due to the disturbance of inter-atomic fields by atomic collision.

Line Absorption Spectra of Excited Atoms

An excited atom is one having an outer electron in an orbit other than its normal orbit. We shall first consider atoms for which the outer electron is in the orbit of next higher energy level than that of the normal position. For hydrogen this is the second ring; for the alkalis, the orbit 2 p_1 or 2 p_2; and for the metals of Group II of the periodic table, the orbit 2 p_2. In the latter case we shall neglect consideration for the present of the orbit 2 p_3 which lies between 1 S and 2 p_2.

Two means have been already discussed by which the valence electron may be ejected to this second orbit. First, as the immediate result of an electron collision at the resonance potential or as an indirect result of recombination, following ionization, and return toward normal, the electron may temporarily assume a position in the second orbit. Second, the electron may be ejected to the second orbit directly by absorption of radiation of such frequency as $1\ s - 2\ p$ or $1\ S - 2\ p_2$ as discussed in the preceding section, or indirectly by the absorption of any radiation of the type $1\ s - mp$ followed by subsequent emission of a line in a series converging at 2 p. A third method, which is discussed in Chapter VII, involves a consideration of the effect of elevated temperatures. There is evidence that merely heating a gas drives a valence electron to an outer orbit.

The electron once in the second orbit does not in general remain there long, and if undisturbed falls into the normal orbit emitting the first line of the principal series — the single-line spectrum — as shown in Chapter V. The question as to the length of time τ the second orbit is occupied is a most fundamentally important one and will be considered below.

The Measurement of τ

Suppose in the case of mercury that the atom remains in the excited condition for exactly τ sec., and that the time required for a stimulus to thus activate the atom and the time during which radiation is subsequently emitted is small compared to τ. That is, suppose the time required for any interorbital transition were negligibly small compared to the time during which an electron occupied an outer ring such as the 2 p_2 orbit. This being true we shall consider what may be done with a unidirectional stream of mercury vapor issuing from a properly designed nozzle, as shown in Figure 16. This stream is illuminated at b by a small diaphragmed beam of radiation of wave-length λ 2537, the cross

section of the beam being represented by *c*. The atoms are accordingly stimulated at *b* and for each excited atom a valence electron is ejected to the 2 p_2 orbit, as a result of the exciting radiation. On account of the velocity of translation of the atoms, which may be determined by a measurement of the temperature of the boiling vapor or by other means, the atoms travel to the position b' before returning to the normal state. Accordingly at b' there should be an emission of the line λ 2537 and the distance b to b' gives a measure of the time τ in the excited state.

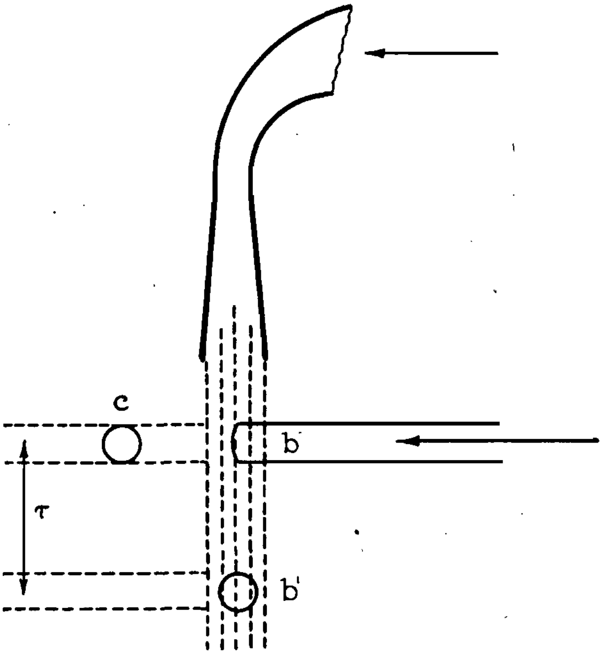


FIG. 16. Unidirectional stream of mercury vapor.

Unfortunately, although such an experiment yields interesting results which will be considered in the latter part of this chapter, it has no bearing upon the life of an excited atom. That this is true is evident from a consideration of the molecular velocities involved. The most probable velocity, as follows from the kinetic theory of gases, is given by the expression $v = 12900 \sqrt{T/M}$ where T is the absolute temperature and M the molecular weight of the gas. For mercury at 500° abs we obtain a velocity of 2×10^4 cm/sec. Hence in 10^{-8} sec., which, as will appear, is the probable order of magnitude of the result desired,

the atoms would have traveled the almost imperceptible distance 2×10^{-4} cm. Furthermore, aside from the above and the question of the distribution of velocities in the stream, and the fact that the time τ is a mean phenomenon analogous to mean free path, etc., other difficulties may arise which make such an experimental arrangement impossible. For example some of the radiation emitted when an atom returns to the normal state may be absorbed by a neighboring atom so that the original radiation is passed on successively by many atoms, if the pressure is high, before it finally escapes from the stream. Horton and Davies observed that radiation produced at the resonance potential, 21.2 volts, in helium, in one side of a well-shielded U-tube was passed on from atom to atom, finally appearing at the other end of the tube. The phenomenon is well known in the study of resonance radiation where the entire bulb is filled with a glow by a narrow beam of exciting radiation. If this effect were predominant, measurements such as the above would simply give the average length of time that the radiation in a particular apparatus may be passed on from atom to atom.

We define τ as the *average* time during which an electron remains in an outer orbit of an atom. If at a given time $t = 0$, we have N_0 excited atoms, then the number N which remain in the excited state after t seconds have elapsed is

$$N = N_0 e^{-2\alpha t},$$

where α is a constant. It is at once apparent that the *average* value of t for all the atoms is given by $\tau = 1/2\,\alpha$.

The constant α may be determined experimentally in the following manner, where we shall consider, for simplicity of explanation, the λ 2537 line of mercury. A canal ray tube is employed which is divided into two chambers, A and B, separated by the cathode through which an extremely small hole or slit is cut. The vapor is excited in chamber A by electronic bombardment at several thousand volts. The resulting positive ions are driven to the cathode and some of these are projected with high velocity through the hole into the chamber B. This latter is maintained at the highest possible vacuum by vapor pumps, liquid air, etc., so that no disturbing collisions will occur here. The cathode acts a shield to the region B, keeping away stray electrons. Yet it is found that the atoms in B are neutral. This means that each atom projected through the chamber B, as the result of the velocity which it accumulated while an ion in chamber A, recombined somewhere in A, probably very close to the cathode. Let us assume tentatively that at

the instant each now neutral atom penetrates chamber B, it is in a state to emit λ 2537; that is, a valence electron lies in the 2 p_2 orbit. At this point, for some few atoms, the valence electron drops to the normal 1 *S* orbit, the process occurring for all the atoms, relative to time, as indicated by the above equation. Since, however, the atoms all have a very high unidirectional velocity, the resumption of the normal condition occurs over a considerable length of space for the entire group of atoms. As each return to normal is accompanied by the emission of a quantum of λ 2537, we obtain a streak of emitted radiation, which may be several cm in length for a light element, the intensity of which decreases, as follows from the above, proportionally to $e^{-2\alpha x/v}$, where x is the distance of penetration in B and v is the velocity of the stream. This velocity may be found by observation of the Doppler effect in the emitted radiation.[27]

Wien[28] has made extensive measurements on hydrogen, nitrogen and oxygen, but at present the experimental difficulties have not permitted the use of vapors such as mercury.[29] In general the theory is not quite as simple as that outlined above. The atoms entering the chamber B are in excited states corresponding to the outermost quantized orbits. They are therefore capable of emitting any of the arc lines. The intensity of H_β (for example) representing an interorbital transition between orbits of quantum numbers 4 and 2 first increases slightly and then decreases in accordance with the law already given. Mie[30] shows such an effect is to be expected.

The value of 2 α is found to be of about the same magnitude for different lines even with different elements. For the β and γ lines of hydrogen Wien observed $2\,\alpha = 4.35 \cdot 10^7$ sec^{-1} or $\tau = 2.3 \cdot 10^{-8}$ sec. Dempster[31] obtained for H_β, $\tau = 5 \cdot 10^{-8}$ sec.

The conception of the occupancy of an outer orbit for an appreciable time has as an analogue the emission of damped vibrations in accordance with the ideas of classical dynamics. Thus the damping constant for a radiating electron vibrating about its position of equilibrium may be shown to have the form

$$2\,\alpha = \frac{8\,\pi^2 e^2 \bar{v}^2}{3\,mc^3}\,.$$

[27] Wood has described several methods (Proc. Roy. Soc., 99, pp. 362–371, 1921) for the measurement of the very short time interval between the absorption of light by phosphorescent substances and its re-emission. Possibly the modification of the Abraham and Lemoine method therein described could be applied to the measurement of τ for resonance radiation.

[28] Ann. Physik, 60, pp. 597–637 (1919); 66, pp. 229–36 (1921).

[29] In part probably because of the very high voltage necessary to produce a sufficient velocity of the heavy mercury ions. See Fig. 45 (Appendix I).

[30] Ann. Physik, 66, pp. 237–60 (1921).

[31] Phys. R., 15, pp. 138–9 (1920).

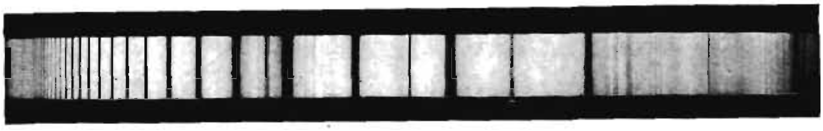


FIG. 17. Spectrum of Zeta Tauri from H_γ to limit of Balmer series (last line showing H_{31}) made with 37½ inch reflector. These hydrogen lines are all absorption lines, reversed against the continuous background of the stellar emission spectrum.

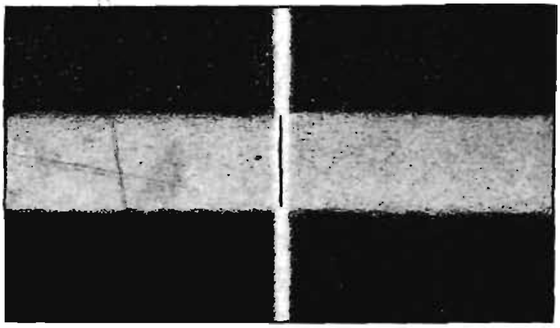


FIG. 18. Reversal of hydrogen alpha in the laboratory.

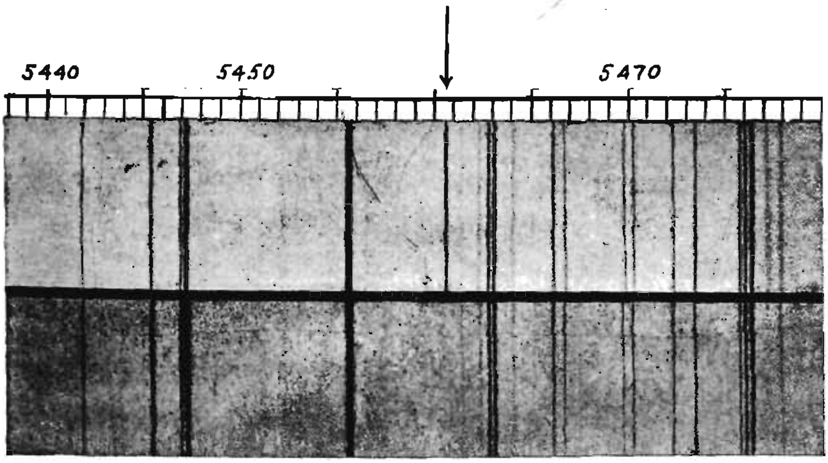


FIG. 19. The upper spectrogram shows the reversal of the mercury line λ 5461, $2p_1 - 1s$, against the solar spectrum. The lower spectrogram shows the solar source alone.

This gives for the average duration of the emission $\tau = 1/2\alpha = 2 \cdot 10^{-8}$ sec. for H_α. In general we may conclude that τ is of the order 10^{-8} sec.

Absorption of Subordinate Series Lines

It is readily seen by referring to the energy diagrams, Figures 4 to 9, that an atom having an electron in the second or 2 *p* ring is capable of absorbing any radiation belonging to spectral series which converge at this energy level. The process is identical with that discussed in the preceding section, except all the transitions take place from the second instead of first orbit. This is the explanation of the appearance of the Balmer series of hydrogen as absorption lines or of the frequently observed reversals of lines of the subordinate series in the case of the alkalis and alkali earths. Figure 17 shows the spectrum of Zeta Tauri in which lines of the Balmer series from H_γ to H_{31} appear sharply reversed. This illustration is from a photograph made by Dr. R. H. Curtiss, University of Michigan, for the authors. The absorption is produced by a stratum of excited hydrogen atoms against the continuous emission spectrum from an interior layer in the star.[32] The solar spectrum also shows as Fraunhofer lines many lines belonging to subordinate series, for example, the C line which is H_α. The literature abounds with examples of such reversals in the arc. Meggers[33] mentions the reversal of λ 8183. λ 8195, 2 *p* − 3 *d*, the first pair of the 1st Subordinate series of sodium. Many similar cases are to be found in Kayser's tables. The arc reversals, which appear as narrow black lines on the bright, wider background of the emission spectra are readily observed visually in a cored carbon arc. Usually they flash on for only a few seconds: it is very difficult to obtain more than a momentary appearance of a large number of such absorption lines at the same time. This momentary character is due to the constant shifting of the envelope of absorbing and excited vapor immediately surrounding the arc.

Spectroscopists have in the past made little differentiation between the reversal of a line of a principal series and a line of a subordinate series. In fact the principal series of an alkali has been incorrectly called its Balmer series because its lines are all easily absorbed, giving a spectrum resembling the Balmer lines in the spectra of certain stars (compare Figures 12, 13, and 17). The physical mechanisms, however, producing the Fraunhofer C and D lines are entirely different, a fact readily recognized when one attempts to show in the laboratory the Balmer absorption spectrum of hydrogen. No one has ever produced in

[32] See Chapter VII.

[33] Bur. Standards Sci. Paper, No. 312.

the laboratory a subordinate series spectrum at all resembling that given in Figure 17, although it is not difficult to obtain such a spectrum for a principal series.

The authors have devised many methods for producing this peculiar type of absorption — so far without much success. The resonance potential of the hydrogen atom is 10.2 volts. Hence if a hydrogen atom collides with a 10.2 volt electron, it is capable for an instant of absorbing a line of the Balmer series. A similar condition in reference to the subordinate series holds for sodium bombarded by 2.1 volt electrons. Another suggested method is to illuminate sodium vapor with intense radiation from a sodium flame. The resulting absorption of the D-lines should activate the sodium atoms so that they would be capable of absorbing the subordinate series. A long train of sodium flames should be capable of showing this absorption. Zahn,[34] from photometric measurements and determinations of the quantity of sodium present in a flame, has computed that each sodium atom emits about 2000 quanta of D-radiation per second. If the time during which the atom remains in the active state is 10^{-8} sec., an atom on the average, per second, has an electron in the 2 p ring for 2000×10^{-8} or about 10^{-5} sec. In other words at any instant about 1 in 50,000 sodium atoms is capable of absorbing subordinate series lines. This proportion should be sufficient to show some effect in a long train of flames.

While these experiments bearing directly upon the quantum theory of absorption have not as yet yielded satisfactory results, there are many indirect indications of its validity. It is very difficult to produce a sufficiently long column of vapor heavily bombarded by low speed electrons at the resonance potential. However, with a Geissler tube, and high potential, a very long column of excited vapor may be obtained. The objection to this method of activation is that the atoms are emitting the complete spectrum and hence electrons are to be found in every possible orbit instead of the second orbit only. Since, however, the first fundamental line of the type 1 s — 2 p is emitted strongly, the orbit 2 p is occupied to some extent and absorption of the subordinate series should occur. In general the absorption of, for example, 2 p — 3 d, is obscured by the emission of this line by the gas but there are methods for detecting it.

Wood[35] has described a very simple method for observing the absorption of the Balmer line H_α in hydrogen. Using a long discharge tube arranged for end-on observation it is noticed that the color of the dis-

[34] Verh. d. Physik. Ges., 15, pp. 1203–14 (1913). [35] "Physical Optics," 2d Ed.

charge is rose-red as viewed through the side of the tube, but is bluish-white when viewed along the axis. In the latter case the red line has been absorbed by the long column of excited vapor. A similar phenomenon may be observed with other gases and vapors.

Ladenburg[36] has obtained a reversal of H_α by the following method. Two long discharge tubes are mounted on a common axis and arranged with windows for end-on observation.[37] These are excited in series by an induction coil. The pressure in the rear tube is high so that broad intense emission lines are produced. The vapor in the front tube both emits and absorbs H_α, but by proper regulation of the pressure a narrow reversal may be obtained, as shown by Figure 18. This illustration is a drawing, as the actual photographs of the phenomenon, though conclusive, were not very satisfactory for reproduction. The band of light is the broad H_α line emitted by the rear tube at high pressure. The long narrow line comes from the front tube. A small portion of this is reversed where it crosses the emission band of the rear tube. When a pulsating discharge is used, it is necessary to have both tubes glow at exactly the same instant. If, however, a direct current discharge is employed for the absorption tube, a continuous source, such as an electric lamp, may be used for the background. From photometric measurements upon the brightness of (1) the source alone, (2) the glowing absorption tube alone, (3) the two in combination, it is possible to compute the absorption coefficient of the gas for the various spectral lines. By employing high dispersion and resolution, Ladenburg and others have determined the absorption curve over the single line H_α, and find that in general almost complete absorption occurs. None of the light of wave-length H_α from the background penetrates through the excited vapor.

Metcalfe and Venkatesachar,[38] using a tube containing mercury vapor which was excited by a small current above the ionization potential, observed, photometrically, absorption of the following and other mercury lines.

λ	Notation	Remarks
5461	$2\,p_1 - 1\,s$	strong
4359	$2\,p_2 - 1\,s$	"
4047	$2\,p_3 - 1\,s$	"
3342	$2\,p_1 - 2\,s$	very strong
3663	$2\,p_1 - 3\,d$	strong

[36] Verh. d. Physik. Ges., 12, pp. 54–80 (1910); pp. 549–564 (1910).
[37] This experiment is most beautifully made by use of discharge tubes with windows *fused on* by the Fairchild method, cf. J. Optical Soc. Am., 4, p. 496 (1920).
[38] Proc. Roy. Soc., 100, pp. 149–66 (1921).

They state that the absorption of λ 2537, 1 S — 2 p_2, is not increased when the vapor is luminous. It is evident that such should be the case. If any perceptible change could be detected the luminous vapor should show less absorption for this line in proportion to the ratio of the number of excited to normal atoms — actually an extremely small quantity. These investigators succeeded in obtaining complete reversal of the lines 2 p_1 — 1 s and 2 p_2 — 1 s. The lower spectrogram of Figure 19 was obtained by sighting directly on the sun and shows the Fraunhofer lines, while for the upper spectrogram a column of excited mercury vapor was interposed in the line of sight. The reversal of the green mercury line 2 p_1 — 1 s, λ 5461 A, shows clearly in the upper spectrogram.

One of the most interesting contributions to this subject has been made recently by Fuchtbauer.[39] He employed a double-walled, long cylindrical tube of quartz between the two walls of which a mercury arc was excited. In the central open space coaxial with the discharge tube was mounted a second closed quartz tube fitted with windows for end-on observation. This second tube contained mercury vapor the pressure of which could be regulated. The emission tube was further jacketed outside with a layer of mercury which acted as a reflector concentrating the radiation on the interior, and the entire system was cooled by an ice bath. When the vapor pressure in the inner tube was adjusted to that corresponding to about 35° C, this vapor became intensely luminous, emitting all the arc lines of mercury, although it had no connection whatever with an exciting potential.

This fact is precisely what one should expect on the basis of the quantum theory of spectroscopy. We shall analyze these results in detail. The atoms in the inner tube are first excited by radiation of some frequency belonging to a series converging at 1 S. There are two such series 1 S — mP and 1 S — mp_2. According to the theory an electron would be ejected to an mP or an mp_2 orbit by absorption of the corresponding spectral line in these two series. The first line of the first series is λ 1849. The first two lines of the second series are λ 2537 and λ 1292. The radiation from the enveloping quartz lamp must pass through two quartz walls before it reaches the vapor in the inner tube. Fused quartz is opaque to all lines of these series except λ 2537 and to some extent λ 1849. Fuchtbauer states that practically no light of wave-length λ 1849 was transmitted. Certainly the radiation of this wave-length would be weak compared to λ 2537 and we shall omit its consideration. In so doing, however, the bearing of the theory upon

[39] Physik. Z., 21, pp. 635–8 (1920).

the observed phenomenon is unaltered. A similar analysis may be carried through by the reader, admitting the presence of λ 1849.

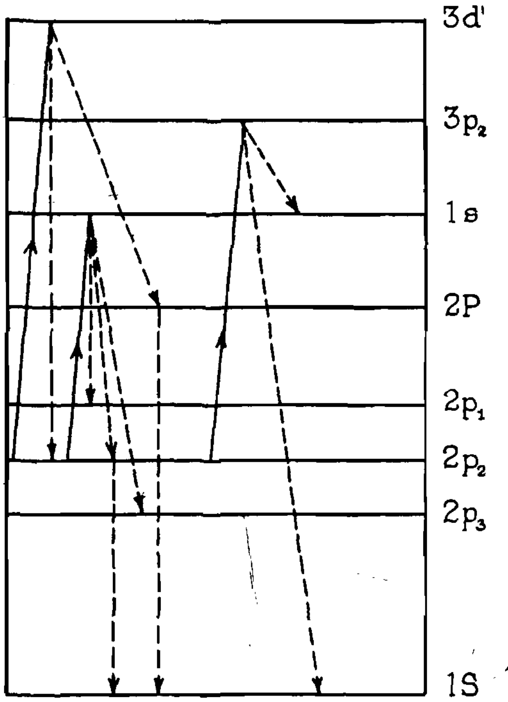


FIG. 20. Small portion of energy level diagram for mercury.

Accordingly the radiation chiefly effective in initially exciting the vapor is 1 S − 2 p_2, λ 2537. This radiation is absorbed by the vapor and each excited atom has an electron in the 2 p_2 orbit. Before the electron has time to return to the 1 S orbit, with a resulting emission of λ 2537, it absorbs a quantum of energy of some frequency belonging to a series converging at 2 p_2. This radiation is readily transmitted through the quartz. The azimuthal quantum number of the 2 p_2 orbit is 2. Hence since there is no disturbing electrostatic or magnetic field, this absorption, by the Bohr principle of selection, will displace the electron to an orbit where the azimuthal quantum number is either 1 or 3, that is to a *ms*, *mS*, *md*, or *mD* orbit of higher energy level, and the line absorbed from the exciting radiation will belong to one of the four series which converge at 2 p_2. The process is illustrated by the energy level diagram, Figure 20, on which a *few* of these transitions are indicated.

Suppose the atom absorbed the line $2\ p_2 - 3\ d'$, λ 3126. The electron is accordingly displaced to the $3\ d'$ orbit and the atom is in a position to absorb lines of the Bergmann series. This process may be continued with a multitude of variations up to the point where the electron is completely removed and the atom is ionized. At any stage in the process the electron if undisturbed may return to normal either directly or by successive steps, emitting various lines of the arc spectrum, some of which are shown by dotted lines in Figure 20. If the atom with the electron in the $2\ p_2$ orbit absorbs the line $2\ p_2 - 1\ s$, it is then in a position to emit the lines $2\ p_1 - 1\ s$ or $2\ p_3 - 1\ s$ and the electron falls to the $2\ p_1$ or $2\ p_3$ orbits respectively. These two configurations possibly constitute metastable forms of the mercury atom just as in the case of helium, where we found that the orbits $2\ S$ and $2\ s$ represented metastable forms of this element. Lines of the wave numbers $\nu = 1\ S - 2\ p_1$ and $1\ S - 2\ p_3$ are not observed in the arc spectrum of mercury, showing that an electron in either the $2\ p_1$ or $2\ p_3$ orbit may reach normal only by absorption of energy and hence by passing through an orbit corresponding to a greater energy level.

If the atom with an electron in the $2\ p_2$ orbit absorbs the line $2\ p_2 - 3\ d'$, λ 3126, and then emits the line $2\ P - 3\ d'$, λ 5770, the electron is transferred to the $2\ P$ orbit. It is now in a position to emit $1\ S - 2\ P$, λ 1849. Also transitions are readily apparent by which the electron may be ejected to the $3\ p_2$ orbit where it is in a position to emit the line $1\ S - 3\ p_2$, λ 1292. Accordingly by this simple process lines of very much higher frequencies than those present in the exciting source are easily stimulated. This fact alone should be sufficient argument for discarding Stokes' law[40] which now has as many exceptions as verifications, and is of little value, although often quoted. It should be noted that the production of radiation by the absorption of radiation of *lower* frequency is in accord with the principle of conservation of energy. In the above example we have several frequencies transformed into one of higher value, subject to the energy relation $\Sigma_i ch\nu_i = ch\nu =$ energy, where $\nu > \nu_i$.

The entire experiment just discussed depends upon the absorption of the fundamental line $1\ S - 2\ p_2$, λ 2537. When this line was cut off by a thin cylinder of glass, no effect whatever could be detected. The glass transmits freely the lines of series converging at $2\ p_2$, but since with the glass, there is no radiation transmitted, through the absorption

[40] This law states that the emitted radiation can not have a shorter wave-length than that of the stimulus.

of which the electron can reach the 2 p_2 orbit, the vapor in the inner tube is unaffected.

We have already pointed out that with helium, when an electron is displaced from its normal orbit it tends to assume either the 2 *S* or 2 *s* orbits, which are the basic energy levels for the two systems of spectral series for this element. Apparently these orbits may be occupied for a much greater length of time than 10^{-8} seconds.[41] Hence lines in series converging at either 2 *S* or 2 *s* should readily show absorption, as is apparent from Figure 10. Paschen[42] has observed absorption of the lines 2 *S* − 2 *P*, λ 20582, and 2 *s* − 2 *p*, λ 10830, in a Geissler tube excited by a weak current. The stimulating current causes ionization of the gas which is followed by recombination. The electron returns toward normal by successive interorbital transitions, with resulting radiation, ultimately reaching the orbits 2 *S* or 2 *s*, which are occupied for an appreciable time. In this state the two most prominent absorption lines should be those observed by Paschen. The effect is of course assisted by any electronic impact at the resonance potential in *which case an electron may be ejected directly to the 2 S or 2 s* orbits.

A simply ionized atom should be capable of absorbing lines of the enhanced spectrum. The ionized alkali earths should readily show absorption for the pair 1 $\mathfrak{S}$ − 2 $\mathfrak{P}_{1,2}$, and for higher terms in this series. No laboratory experiments have been performed to test this fact, but scattered observations point to its truth. King[43] finds that both members of this doublet for calcium, λ 3968 and λ 3933, may appear reversed in furnace spectra. These lines are respectively the H and K Fraunhofer absorption lines in the solar spectrum. The corresponding pairs for strontium and barium also appear as absorption lines in the sun. The pair is reversed in the spark spectra of Mg, Ca, Sr, and Ba.

We may have excited ionized atoms which behave precisely like the excited un-ionized atoms discussed in the foregoing paragraphs. With certain types of excitation the remaining valence electron for the atoms of metals of Group II may be ejected to an outer orbit such as 2 $\mathfrak{P}$, under which condition the atom absorbs lines of the enhanced subordinate series. The following partial list of reversals of enhanced lines of subordinate series is typical.[44]

[41] See pages 73 and 93.
[42] Ann. Physik, 45, pp. 625–56 (1914).
[43] Astrophys. J., 51, pp. 13–22 (1920).
[44] Compiled mainly from Kayser's tables. These reversals are, however, a matter of common experience.

TABLE XVIII

Element	Notation	λ	Source
Mg..................	$2\mathfrak{P}_1 - 3\mathfrak{D}$	2798	Spark
	$2\mathfrak{P}_2 - 3\mathfrak{D}$	2790	"
	$2\mathfrak{P}_2 - 2\mathfrak{S}$	2928	"
Ca..................	$2\mathfrak{P}_1 - 2\mathfrak{S}$	3737	"
	$2\mathfrak{P}_2 - 2\mathfrak{S}$	3706	"
	$2\mathfrak{P}_1 - 3\mathfrak{D}_2$	8498	Sun
	$2\mathfrak{P}_1 - 3\mathfrak{D}_1$	8542	"
	$2\mathfrak{P}_2 - 3\mathfrak{D}_2$	8662	"
	$2\mathfrak{P}_1 - 4\mathfrak{D}_2$	3181	Spark
	$2\mathfrak{P}_1 - 4\mathfrak{D}_1$	3179	"
Sr..................	$2\mathfrak{P}_1 - 2\mathfrak{S}$	4305	"
	$2\mathfrak{P}_2 - 2\mathfrak{S}$	4161	"
	$2\mathfrak{P}_1 - 4\mathfrak{D}_2$	3475	"
	$2\mathfrak{P}_1 - 4\mathfrak{D}_1$	3464	"
Ba..................	$2\mathfrak{P}_1 - 2\mathfrak{S}$	4525	"
	$2\mathfrak{P}_1 - 4\mathfrak{D}_2$	4166	"
	$2\mathfrak{P}_1 - 4\mathfrak{D}_1$	4130	"
	$2\mathfrak{P}_2 - 4\mathfrak{D}_2$	3891	"
	$2\mathfrak{P}_1 - 5\mathfrak{D}_1$	2634	"
	$2\mathfrak{P}_2 - 5\mathfrak{D}_2$	2528	"

Reversals of enhanced lines are of particular interest in celestial spectroscopy, where they furnish an indication of stellar temperatures as indicated in the latter part of Chapter VII.

We shall consider briefly some of the rather speculative deductions to be drawn from experiments with a stream of mercury vapor. Phillips[45] employed a long inverted quartz U-tube, closed at each end. The leg containing mercury was heated to 350° C, while the other leg into which the mercury distilled was water cooled. Just above the surface of the boiling mercury a beam of radiation of wave-length λ 2537 was projected through the vapor. The entire tube was immediately filled with luminous radiation. Figure 21 shows a spectrogram of the fluorescent light. The resonance line λ 2537 is predominant, and in addition we have a band of radiation in the extreme violet and another band, which accounts for the visible luminosity, in the green. The faint lines

[45] Proc. Roy. Soc., 89, pp. 39–44 (1913).

on the right are due to stray radiation from the source. Wood[46] by a very ingenious method found that the luminosity began to appear about 1/16000 second after the exciting stimulus was applied. At very high pressure the time could be reduced to 1/40000 second. The fact that the time is so much greater than 10^{-8} second suggests, and the appearance of a band spectrum shows, we are dealing with a new phenomenon. Franck and Grotrian[47] have repeated these experiments, with various modifications, from which they have drawn conclusions which will be reviewed in the following paragraphs.

In general band spectra are attributed to molecules. Excited atoms possess an electron affinity which enables them to unite with other atoms forming compound molecules. The subject of electron affinity is briefly considered in Chapter VIII. We may here state that an atom possessing an electron affinity may attract an electron and become a negative ion. Work must be done upon the negative ion to reduce it to a normal atom. Metals and the rare gases in their *normal* states do not possess an electron affinity. We shall first consider the excited helium atom for which we assume that there is one electron in orbit of quantum number 1 and one electron in orbit of quantum number 2, the orbits being coplanar. The total energy of this configuration, obtained by means of Equations (50) and (51) is as follows:

$$W = W_p + W_q = -4\,Nhc - 0.25\,Nhc = -4.25\,Nhc. \qquad (71)$$

The helium negative ion may be assumed to contain one electron in orbit of quantum number 1 and two electrons in orbit of quantum number 2. Whence by means of the same equations we find:

$$W' = W'_p + W'_q = -4\,Nhc - 0.28\,Nhc = -4.28\,Nhc. \qquad (72)$$

The second state is accordingly stable. Work has to be done upon the helium ion thus formed to remove the extra electron. This work amounts to 0.03 *Nhc* ergs or 0.4 volts.

We have noted the extreme stability of a pair of electrons grouped about a single point charge nucleus. The normal helium structure is characteristic of the *K*-ring of all the elements. This tendency to grouping in pairs appears now in the formation of negative ions, but the stability of such an outer structure built about not only a nuclear charge but other electrons is not very great. We have in these negative ions, formed from excited atoms, a *metastable* compound of an atom

[46] Proc. Roy. Soc., 99, pp. 362–71 (1921).
[47] Z. Physik, 4, pp. 89–99 (1921).

and an electron, with an outer structure resembling normal helium,[48] and an electron defect in the next to the outer shell which normally is the outer shell.

If an excited helium atom which has not picked up an extra electron collides with a similar atom, the electron affinity of each atom causes an attraction resulting in the formation of He_2. Lenz[49] has already attributed the excitation of a band spectrum of helium in a strong discharge to the presence of the helium molecule.

There is no tendency for a normal argon atom to become negatively charged. However, in the Moore tube light, the pressure at the anode may be double that at the cathode (measurable with an ordinary mercury manometer) on account of the drift of *negatively* charged argon atoms. The argon atom is excited and an electron is driven to the second orbit. In this condition it attracts another electron, forming a metastable configuration with a helium-like outer structure and an electron defect in what was normally the outer shell, the whole being a negative ion.

Franck and Grotrian suggest that in a manner similar to the formation of negatively charged atoms of rare gases, negatively charged atoms of metals may be produced. The valence electron of a sodium atom, for example, may be ejected to the 2 p_2 orbit, where the atom as a whole may possess an electron affinity and may become a negative ion, while there is no tendency to such a condition as long as the valence electron remains in its normal orbit.

The mercury stream experiments are accordingly interpreted as follows. The radiation of wave-length λ 2537 is absorbed by the atom with a resulting ejection of an electron to the 2 p_2 ring. Ordinarily this electron would return to normal in 10^{-8} seconds with an emission of the line λ 2537. Practically no displacement of the illuminated spot would be detectable. Franck and Grotrian confirmed this fact by employing a low pressure in the absence of any foreign gas. At higher pressures, however, the short-lived excited mercury atom may collide with a normal mercury atom, forming the molecule Hg_2. The excited atom which possesses an electron affinity is the negative component in this compound. It has in the union a helium-like outer shell, completed by a valence electron of the normal atom, and an electron defect in the next to the outer shell. The normal atom is the positive constituent like Na in NaCl. This new molecule possesses a temporary stability

[48] Possibly more exact considerations would make the resemblance closer in that the orbits of the outer pair would be crossed, as illustrated by Figure 11.
[49] Verh. Physik. Ges., 21, p. 632 (1919).

and the duration of the after glow in the stream is a measure of its life. A band spectrum results from the movement of electrons and nuclei within the *molecule*. Dissociation arising in collision either with normal mercury atoms or foreign gas, permits the electron in the excited atom to return from 2 p_2 to the 1 S orbit, thus emitting λ 2537, as shown by Figure 21. These conclusions have been fairly definitely verified by several experiments which cannot be discussed here.

The foregoing, while it apparently explains one means of forming molecular compounds, is not the complete interpretation of the experimental facts. Sodium vapor at fairly high density shows thousands of fine absorption lines which Wood[50] believes are the complement of the fluorescent spectrum excited by white light. Light may be absorbed by sodium vapor from a nearly monochromatic source in which there is no frequency corresponding to any line of the principal or other series of sodium. Hence the presence of the absorbing molecules cannot be attributed to the preliminary activation of the atoms by the source of radiation. Strong monochromatic illumination of sodium vapor by a red or green line, *not* present in the arc spectrum of sodium, gives re-emission of that line and a series of lines at intervals of about 37 A on each side of the exciting line. These spectra are almost the exact counterpart of the phenomena obtained with iodine. The theory that they likewise are due to a diatomic molecule is supported by this similarity, but the presence of the molecules again cannot be attributed to activation of the atoms by light which they are not capable of absorbing. Likewise with mercury fluorescence it is found that the most effective illumination is not light near λ 2537 but of a higher frequency, again in no relation to the series lines of the mercury atom. We accordingly see that molecular compounds may be formed *without* excitation of the atoms by light of a series converging at 1 s or 1 S. It appears necessary to assume that the vapors contain molecular formations whether or not they are illuminated. Wood states that the fluorescence of mercury appears only in case of vapor freshly liberated from the fluid metal. Fluorescence cannot be excited in a bulb of cooling (hence condensing) mercury vapor, containing an excess of mercury at the same temperature at which it is brilliant in case the temperature is rising, accordingly where evaporation is taking place. Apparently then molecular compounds such as Na_2, Hg_2 may be evaporated from the liquid surface. Now if Franck and Grotrian's explanation of the structure of these compounds is correct, that is if Hg_2 consists of an

[50] "Physical Optics," 2d Ed.

excited and a normal atom, simply boiling mercury briskly should produce an emission of $1\ S - 2\ p_2$, λ 2537. Decomposition of the metastable compound Hg_2 should release an atom having an electron in the $2\ p_2$ ring which on returning to normal emits this fundamental line. A six hour exposure to a vessel of boiling mercury, by Dr. Meggers and the authors, failed to show a trace of this line. The experiment, however, is worthy of further thought.

The entire subject of the behavior of excited atoms is a new field of research which promises interesting development. No doubt the chemist of the future will deal familiarly with such compounds as the helides, argides and so on.[51]

[51] Since this book has been in press a note by A. S. King, Proc. Nat. Acad. Sci., 8, pp. 123–5 (1922), has appeared, in which he makes the statement that the subordinate series of Na, K, Rb, and Cs have been reversed in furnace spectra obtained by heating the vapor to a high temperature. This is a confirmation of the theory of absorption by excited atoms where the excited atoms are produced by temperature, *i.e.* by the third method mentioned at the beginning of the section on "Line Absorption Spectra of Excited Atoms."

A very important paper by Franck has just appeared, Zeit. Physik, 9, pp. 259–66 (1922), on the subject of excited atoms. Klein and Rosseland have suggested that a slow-moving electron, in collision with an excited atom, may gain kinetic energy while the atom is assuming its normal state, no radiation being emitted in the process. This is the converse of excitation by collision. Franck has extended this idea to collisions between excited and unexcited atoms, thereby obtaining a *partial* explanation of the weakening of resonance radiation by the presence of foreign gas. The theory is also used to explain the appearance of Hg λ 2537, $1\ S - 2\ p_2$, when Hg vapor is excited by λ 1849, $1\ S - 2\ P$. This may require a transition without radiation from the $2\ P$ state to the $2\ p_2$ state. Cario, working in Franck's laboratory, has shown that thallium lines appear in mixtures of Tl and Hg vapors excited by λ 2537, which is interpreted to mean that excited Hg atoms can give up their energy to unexcited Tl atoms with which they collide. Other applications are to the sensitizing of photographic plates by staining, to the bright fluorescence of almost all substances at low temperature, and to the Maxwell velocity distribution in the emission of electrons from heated surfaces.

Chapter V

Line Emission Spectra of Atoms

We have seen that when an electron in an atom is transferred from an outer to an inner orbit, energy is released as a quantum of radiation of wave number ν. If W is the total energy of the atom corresponding to the initial configuration and W' the energy of the final configuration, the wave number of the emitted radiation has the value:

$$\nu = (W - W')/hc.$$

The study of line emission is accordingly concerned with the various modes of interorbital transitions of electrons which result in a decrease in the internal atomic energy. Since, however, the *normal* atom in the gaseous state, except for elements having an electron affinity such as the halogens, possesses a minimum of internal energy, it is first necessary to increase this energy before any radiation can be emitted. This is done by ejecting an electron to an outer orbit. Spectroscopy is mainly concerned with the interorbital transitions of a valence or outer electron following such an ejection.

There are at least four general processes through which an atom may be left in a condition such that it is capable of emitting line spectra. A valence electron in an atom may be ejected to an outer orbit (1) by absorption of external kinetic energy at impact, (2) by absorption of radiation as discussed in the preceding chapter, (3) by increase in temperature of the vapor as discussed in Chapter VII. (4) The valence electron of an atom in a molecular compound may be left in an outer orbit or completely removed from the atom in the process of dissociation of the molecule. For example, as shown earlier, the molecule Hg_2 consists of a neutral Hg atom and a Hg atom having a valence electron in the $2\ p_2$ ring. If this molecule is dissociated, the excited atom subsequently should emit the radiation $1\ S - 2\ p_2$. Hydrogen iodide upon dissociation emits the hydrogen spectrum showing that in this molecule the hydrogen atom possesses greater energy than in its normal monatomic state. It is of interest to note that it requires slightly less work

to completely remove the valence electron from the hydrogen atom by dissociation of HI than by ionization of the hydrogen atom directly.[1] Sodium chloride, dissociated in the bunsen flame, emits the spectrum of sodium, to some extent as an immediate result of the dissociation, indicating that in the molecule the sodium atom possesses a greater internal energy than in its normal vapor state. Spectroscopists obtain the spectra of various metals by vaporization and dissociation of their salts in a carbon arc. However, it may not necessarily follow that the process of dissociation leaves the atom in a positively ionized state, even though the complete arc spectrum appears. For example, the dissociation of CdMg may leave one of the atoms as a negative ion.[2] It would be necessary for this negative ion to lose two electrons before it becomes capable of emitting all lines of the arc spectrum. Yet CdMg in an arc would probably show the spectra of both metals.[3] In this and similar cases the dissociation is merely a method for obtaining, by an indirect process, vapor of the metal in the atomic state and the emission phenomena properly fall under the classifications (1), (2), and (3). We should accordingly distinguish between processes of dissociation which leave the atom in a condition to immediately emit radiation and those where the dissociation serves merely for the production of the metal vapor.[4]

Classification (1) broadly interpreted embraces many varieties of energy transfer. Radiation may result from a collision of an atom with an alpha particle, with a heavy ion, possibly with a neutral atom or molecule if the speed is great, but especially with a free electron. Since our quantitative knowledge of emission is almost entirely limited to the effect of collisions between atoms and electrons, we shall confine this section to a consideration of these phenomena. The relation of the processes (2) and (3) to spectral emission are treated in Chapters VI and VII respectively and will be only casually considered for the present. The fundamentally important factor in the ordinary production of spectra is collision between electrons and atoms.

We have seen that a collision between an electron and an atom of the rare gases or metallic elements may be elastic, but at certain well-defined velocities of the impacting electron the collision is inelastic. As

[1] See Table XXXVIII.

[2] A large number of such compounds is given in Gmelin-Kraut's handbook. Probably other more familiar compounds illustrating this point occur in more complex molecules.

[3] Probably any alkali hydride would show both the spectrum of the metal and the atomic spectrum of hydrogen. In this molecule, however, the hydrogen occurs as a *negative* ion.

[4] In general it is probably true that even in such processes as the injection of NaCl in the arc, the salt acts mainly as a carrier for the sodium. The same sodium atom once dissociated from the molecule probably loses and regains its valence electron many times before it leaves the arc.

discussed in Chapter III the energy lost by the electron and absorbed by the atom at an inelastic collision corresponds to either a resonance or ionization potential. If the atom is ionized by the collision, the ejected electron may return to its normal orbit by a variety of interorbital transitions. Each transition results in a decrease in the total energy of the atom and is accompanied by the emission of one quantum of radiation. The various possible steps or energy levels for several typical cases have been considered in the discussion of Figures 4 to 6. If the electron returns from without the atom to the normal state in a single transition, the highest convergence frequency in the spectrum of the neutral atom is emitted. The wave number of this radiation is determined by the quantum relation $hc^2\nu = eV_i \cdot 10^8$, where V_i is the ionization potential in volts. If the electron returns to the normal state by several successive transitions, a corresponding number of quanta of different wave numbers are emitted, of such value that the sum of the quanta equals the total energy of ionization, thus:

$$\Sigma hc^2\nu_k = eV_i \cdot 10^8. \tag{73}$$

With numerous atoms and electrons returning to equilibrium by various paths, we have as the composite result the emission of the complete spectrum of the neutral atom. This by definition is known as the *complete* arc spectrum.

The energy absorbed by the atom during a collision of the resonance type is not great enough to ionize the atom but rather is just sufficient to displace a valence electron to a neighboring orbit of higher energy level. Hence the atom in assuming equilibrium conditions will radiate this energy as quanta of wave number ν such that

$$\Sigma hc^2\nu_k = eV_r \cdot 10^8, \tag{74}$$

where V_r is the resonance potential. The resulting radiation may be termed the *partial* arc spectrum, special cases of which are the so-called single-line spectrum and the two-line spectrum, etc.

The foregoing processes which concern the neutral atom may also apply to an atom which is initially simply ionized. If an ionized atom collides with an electron of sufficient velocity, the collision is inelastic, the atom absorbing the kinetic energy of the impacting electron. If the energy absorbed is sufficient to completely eject another valence or outer electron, the atom is doubly ionized, and the work required to eject this electron, expressed in volts, is denoted by the symbol V_i^* or in general simply V^*. Hence V_i gives the work required to eject the first outer electron from a normal atom, and V_i^* the work required to

eject the second electron *after* the first one has been removed. The second electron may return to its normal state by a variety of interorbital transitions. Each transition results in a decrease in the total energy of the simply ionized atom and is accompanied by the emission of one quantum of radiation. An example of the different energy levels in a typical case (ionized magnesium) is illustrated by Figure 7. If the electron returns from without the atom to the normal state in a single transition, the highest convergence frequency in the spectrum of the simply ionized atom is emitted. The wave number is determined by the relation $hc^2\nu = eV_i^* \cdot 10^8$. If the electron returns to the normal state by several successive transitions, a corresponding number of quanta of different wave numbers is emitted as follows:

$$\Sigma hc^2\nu_k = eV_i^* \cdot 10^8. \qquad (75)$$

Hence with numerous originally doubly ionized atoms, each with an outer electron returning to the normal state of the simply ionized atom by a variety of interorbital transitions, we have as the composite result the emission of the complete spectrum of the simply ionized atom. This by definition is known as the complete spark or enhanced spectrum (of the first type).

As with the neutral atom, electronic collisions may take place in which the energy transfer is not great enough to remove the second electron but rather is just sufficient to displace it to an outer orbit. Hence the ionized atom in assuming equilibrium conditions may radiate this energy as quanta of wave number ν_k such that

$$\Sigma hc^2\nu_k = eV_r^* \cdot 10^8, \qquad (76)$$

where V_r^* is the resonance potential for the simply ionized atom. The resulting radiation may be termed the *partial* enhanced spectrum. No direct measurements of V_r^* have been made, but estimates of its magnitude for several elements may be obtained from spectroscopic considerations, as seen later.

The numerical relationships in the foregoing paragraphs on enhanced spectra require a little further explanation when applied to metals of Group I of the periodic table, since for these, there is but a single valence electron. Removal of the second electron accordingly must take place from what is normally the next to the outer shell, as will be considered later.

We note that a simply ionized atom may emit an enhanced spectrum of the "first type." The above process, however, may be repeated so that a doubly ionized atom should emit an enhanced spectrum of the

"second type," etc. Unfortunately practically nothing is known from the spectroscopic standpoint of these higher types of spark spectra and we shall omit their further consideration.

It is noted in Chapter III that the magnitude of the ionization potential V is small for most elements, of the order 5 to 15 volts. We shall see that V^* also is not great, varying from 10 to 50 volts for the elements concerning which any data exist. Hence 50 volt electrons should be capable of exciting the enhanced spectrum of nearly every element. It has been found, however, that the spectrum characteristic of the neutral atom predominates in the arc, whence the terminology "arc spectrum." For the excitation of the enhanced spectrum, it usually has been necessary to employ a very high potential, thousands of volts, across a spark discharge, whence the terminology "spark spectrum."

Accordingly if spark spectra should appear at low voltage why are they absent or at least weak in the cored carbon arc? There are two reasons for this. First, it is difficult to maintain much of a field in a highly ionized space. If 100 volts is applied to the terminals of the arc, as soon as much ionization occurs, the actual voltage drop *in the arc* falls to a value not greatly exceeding the ionization potential, and the greater portion of the drop is shifted to the leads. This is simply a consequence of Ohm's law, since the "resistance" of the arc itself approaches zero. Secondly and more important, the type of spectrum excited has little immediate relation to the applied voltage, but instead depends upon the speed of the impacting electron. This is a function of the voltage drop *per mean free path*, and for a given applied voltage depends upon the pressure.

Suppose, for example, we had two large, flat, parallel electrodes, separated by 10 cm, such that the applied field produced a uniform potential gradient throughout the 10 cm length. One of the electrodes, *e.g.* a Wehnelt cathode, is assumed to emit electrons. Let us suppose that a potential difference of 100 volts is maintained across these terminals, and the space is filled with mercury vapor at 357° C, that is, at atmospheric pressure. We find, from the kinetic theory, for the mean free path of an electron, to an approximation:

$$\text{mean free path of electron} = l = 1/\pi r^2 n \tag{77}$$

where r is the radius of the gas atom and n is the number of atoms per cm^3. For mercury $r = 1.5 \times 10^{-8}$ cm and in the present example $n = 1.2 \cdot 10^{19}$. Hence $l = 10^{-4}$ cm and the voltage drop per mean free path is accordingly 0.001 volt. The lowest resonance potential of

mercury is 4.9 volts, and electrons having an energy less than this amount collide with the atoms elastically. Accordingly not until each electron has made 4900 collisions has it accumulated enough kinetic energy to produce any disturbance of the mercury atom, and then the energy is only sufficient to displace a valence electron to the 2 p_2 ring. (We have neglected in this simple discussion the fact that the direction of motion of the electron is altered after each collision.) It is evident in this extreme example that very few electrons will ever attain 10.3 volts velocity, sufficient to ionize mercury and produce the arc spectrum, to say nothing of the higher velocity required to excite the enhanced spectrum.

By the time the electron has attained 4.9 volts velocity it has progressed along the tube a distance of 5 mm. Here, to an atom, it gives up its kinetic energy, which is subsequently radiated as a quantum of wave number $\nu = 1\ S - 2\ p_2$, λ 2537. The process is then repeated, so that at every 5 mm along the tube is a stratum of atoms radiating this ultra-violet line. By counting the striae and measuring the applied potential, or preferably by probe wire measurements of potential at each stria, a fairly good determination of the resonance potential may be obtained. The following illustrates such a series of readings made by Grotrian.[5]

Volts.......	15.2	20.0	25.0	29.6	34.2	39.0	43.5	48.0	54.0	59.1	64.2	69.0
Difference...		4.8	5.0	4.6	4.6	4.8	4.5	4.5	6.0	5.1	5.1	5.2

It is of interest that although the light radiated by the mercury atoms lies in the ultra-violet, there is present the green fluorescence characteristic of the molecules formed by the union of an excited and normal atom as discussed on page 104. Hence the striae are readily visible although no ionization is present.

The fact that by increasing the pressure of a metal vapor, all the energy of electronic impact can be forced into a single type of resonance collision corresponding to the lowest resonance potential, is frequently made use of in securing a large number of reversals in the partial current curves[6] even at voltages far exceeding the ionization potential. It is also well known that by employing sodium vapor at high pressure a very efficient "vacuum" arc may be obtained, all the energy of electronic collision going into the production of the D-lines, the first pair of the principal series. The same phenomenon is of course true physically for any vapor, but physiologically sodium stands unique in the close

[5] Z. Physik, 5, pp. 148–58 (1921).
[6] The usual method for determining resonance potentials. See references to Chapter III.

proximity of this line to the spectral region of maximum sensitivity of the eye.

The foregoing discussion clearly shows why spark lines are not strongly present in the ordinary two-electrode arc. Indeed it raises the question as to how any arc lines other than the first term of a principal series, corresponding to the lowest resonance potential, may be present. We may cite five reasons in explanation of this.

(1) The partial pressure of the metal vapor in an ordinary cored carbon arc may be considerably less than an atmosphere — in certain cases possibly only a few mm Hg. The lower the pressure the longer is the mean free path and hence the greater is the chance that an electron accumulates velocity sufficient to ionize. Since the resonance potentials of the atmospheric gases are all high, collision with these gas molecules does not materially affect the ability of the electron to ionize a metal atom.

(2) The phenomenon of absorption of radiation is undoubtedly a controlling factor in the operation of many arcs. This is discussed in some detail in Chapter VI. Collision of an atom and a free electron at the resonance potential gives rise to the first line of an important series, for example $1\ s - 2\ p$ with the alkalis. This radiation is absorbed by a neighboring atom producing an ejection of an electron to the $2\ p$ orbit. Before the excited atom can resume its equilibrium state it is struck by a second electron, and the valence electron is ejected to another orbit of still higher energy level or may be completely removed from the atom. The ordinary mercury vapor arc lamp is readily operated at a pressure greater than one atmosphere and still it emits the complete arc spectrum, although we have just shown that many thousands of collisions must occur before the electron accumulates the velocity corresponding to even the resonance potential. It is safe to conclude that practically no electrons at this vapor pressure have a velocity much greater than 4.9 volts.[7] However, absorption of the radiation $1\ S - 2\ p_2$ following a resonance collision leaves the atom in the excited state where collision with an electron of 5.4 (= 10.3 − 4.9) volts velocity is sufficient to ionize. The ionization may be the result of several absorptions of radiation followed by a single electronic impact, so that in general, as discussed in Chapter VI, ionization may take place in an arc in which there are no electrons having a velocity greater than that corresponding to the resonance potential.

[7] A few electrons very close to the anode and cathode might have higher velocities for reason (5).

(3) A third reason why the complete arc spectrum appears in a two-electrode arc is the phenomenon of successive impact. This is the same in principle as (2). In the case of mercury, for example, the atom is struck by a 4.9 volt electron, and while in the excited state a second electron collides with the atom and raises the valence electron to a higher energy level, ultimately producing ionization.

(4) Although the mean free path of the electron may be too small to permit the accumulation of the ionization velocity over its length, a small proportion of the electrons will travel many mean free paths without collision. At fairly low pressure and high applied voltage this factor may attain considerable importance.

(5) The production of any ionization alters the form of the potential gradient between the cathode and anode. With copious ionization the normally negative space charge around the cathode may be neutralized, eventually becoming positive. A major portion of the potential drop across the arc may then occur within an extremely short distance from the cathode. Hence the emitted electrons have an opportunity for accumulating the ionizing velocity during a mean free path. Under other circumstances a considerable potential drop may occur at the anode with a similar result. Frequently the conditions are such that the total potential drop is divided into two parts, one close to the cathode and the other close to the anode, with little continuous potential variation through the arc itself.

From the above considerations it is evident that no very definite conclusions can be drawn experimentally by observing the voltage necessary to excite particular types of spectrum in a two electrode arc. In general all arc lines and a few fundamental spark lines appear in the arc at 100 volts. Enhanced lines are readily excited in a spark discharge at several thousand volts. Such voltages bear no relation to the minimum energy required to excite these spectra. A knowledge of the actual velocity of the electrons at the instant of collision with atoms is necessary. The following method devised by the authors and Dr. Meggers[8] has yielded definite and conclusive results.

Three electrodes are employed arranged as shown in Figure 22. The central electrode is a heated cathode of tungsten, molybdenum, lime-coated platinum, etc., depending upon the nature of the vapor. Around this is mounted as closely as possible a spiral grid, and outside at a relatively large distance is placed a concentric cylindrical plate.

[8] Foote, Meggers and Mohler, Phil. Mag., 42, pp. 1002–15 (1921); Atrophys. J., 55, pp. 145–61 (1922); Phil. Mag., 43, pp. 659–61 (1922).

The accelerating field for the electrons is applied between the cathode and grid, the latter being in direct metallic contact with the plate. The pressure of the vapor is so regulated that relatively few collisions of electrons and atoms occur in the short space over which the accelerating field is applied. Most of the electrons pass through the grid without collision, thus attaining the full velocity of the impressed field. These electrons then collide with atoms in the large force-free space between the plate and grid, giving up their energy, which is subsequently radiated as line spectra. By observing the minimum potentials at which the different types of spectrum are excited, a direct determination may be made of the amount of energy necessary for their production. The values so obtained in all cases confirm the deductions from the quantum theory. It is of interest to note that with this form of arc the higher series terms are readily photographed. For example, the authors had no trouble in observing such terms as $\nu = 2\,p - 18\,d$ in sodium, rarely if ever detectable in an ordinary arc.

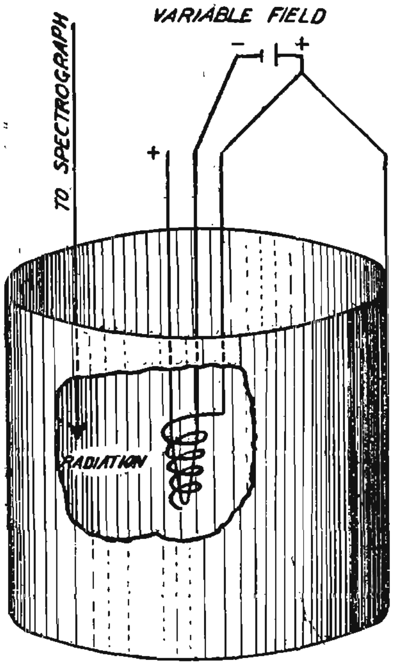


FIG. 22. Arrangement of electrodes for the study of critical voltages required to excite different types of spectrum. The grid must be mounted very close to the cathode.

We shall first consider the metals of Group II of the periodic table, then the alkalis and finally some observations on the rare gases. It must be emphasized that the attack of the problem from our present standpoint is new, practically all work being done during the past year, and hence the data available are rather meager at the present time.

Metals of Group II of the Periodic Table

These metals have two resonance potentials. We should accordingly expect a four stage development in the spectra, a characteristic spectrum at the lower resonance potential, a change at the higher resonance potential, the complete arc spectrum at the ionization potential and the complete spark spectrum at the potential necessary to remove the second valence electron.

As discussed on page 39 the spark spectra of the alkali earths resemble the arc spectra of the alkalis, showing series of doublets as follows:

Principal	$\nu = 1\,\mathfrak{S} - m\mathfrak{P}_{1,2}$	$m = 2, 3, 4,$	(78)
1st Subordinate	$\nu = 2\,\mathfrak{P}_{1,2} - m\mathfrak{D}_{1,2}$	$m = 3, 4, 5,$	(79)
2d Subordinate	$\nu = 2\,\mathfrak{P}_{1,2} - m\mathfrak{S}$	$m = 2, 3, 4,$	(80)
Bergmann	$\nu = 3\,\mathfrak{D}_{1,2} - m\mathfrak{B}$	$m = 4, 5, 6,$	(81)

The highest convergence wave number is $1 \cdot \mathfrak{S}$ and is fairly accurately known for many of these elements, from computation of the observed spectral frequencies. The $1\,\mathfrak{S}$ orbit accordingly represents the normal state or energy level for the ionized atom corresponding to the state $1\,S$ for the normal atom. We shall consider as a typical example the development of the spectra of magnesium. In Table XIX are listed the fundamentally important wave numbers and equivalent voltages, shown graphically in the energy level diagrams of Figures 6 and 7.

Electronic impact at velocities below 2.7 volts gives rise to no emission whatever in magnesium vapor, the collision being elastic. Between 2.7 volts and 4.33 volts an inelastic impact corresponding to the first resonance potential occurs, displacing a valence electron to the $2\,p_2$ orbit. The electron in returning to the $1\,S$ orbit gives rise to the emission of a single line of wave number ν such that $hc^2\nu = eV_r \cdot 10^8$ where $V_r = 2.7$ volts. The wave-length of this line is λ 4571. The first spectrogram of Figure 23, by Foote, Meggers and Mohler, shows this single-line spectrum of magnesium obtained with a total applied potential of 3.2 volts, using the arrangement of electrodes illustrated in Figure 22.

TABLE XIX

Development of Magnesium Spectrum

Series Notation	Wave Number	Volts	Type of Collision	Type of Spectrum
$1\,S - 2\,p_2$	21871	2.70	Inelastic collision, at the lower resonance potential, with neutral atom.	Single-line. Electron is displaced to $2\,p_2$ orbit and the only possible return to normal is by a single transfer to the $1\,S$ orbit.
$1\,S - 2\,P$.	35051	4.33	Inelastic collision, at the higher resonance potential, with neutral atom.	Two lines, $1\,S - 2\,P$ and $1\,S - 2\,p_2$. Electron is displaced to $2\,P$ orbit and must return directly to $1\,S$, since return to $2\,p$ violates principle of selection. Impacts at first resonance potential also occur, giving rise to $1\,S - 2\,p_2$.
$1\,S$......	61672	7.61	Inelastic collision, with neutral atom, resulting in simple ionization.	Complete arc spectrum. One valence electron is completely removed. In returning to normal all interorbital transitions consistent with the principle of selection may take place.
$1\,\mathfrak{S} - 2\,\mathfrak{P}_{1,2}$	35761 35669	4.4	Inelastic collision, with simply ionized atom: the resonance potential of the ionized atom.	Single-line spectrum (d o u b-let). It cannot be produced alone since simple ionization is first necessary, with the resulting emission of the complete arc spectrum.
$1\,\mathfrak{S}$......	121267	14.97	Inelastic collision, with simply ionized atom resulting in ejection of the second valence electron.	Complete enhanced spectrum. This accompanies the arc spectrum since the atom must be first simply ionized. There is no way of maintaining fixed, at reasonable temperatures, an atmosphere of simply ionized atoms. Some are constantly becoming neutral, thus emitting the arc lines.
$1\,\mathfrak{S} + 1\,S$	121267+ 61672	22.8	Inelastic collision, with nuetral atom resulting in ejection of both valence electrons.	Complete enhanced spectrum. The arc spectrum should be present also.

TABLE XIX — *Continued*

DEVELOPMENT OF MAGNESIUM SPECTRUM

Series Notation	Wave Number	Volts	Type of Collision	Type of Spectrum
$La_{1,2}$.	380000	46.9	Inelastic collision, with neutral atom resulting in ejection of an electron from the *L*-orbit.	*L*-radiation, x-rays.
Ka.	95.8 *N*	1299	Inelastic collision with atom resulting in ejection of an electron from the *K*-orbit.	Complete *K*-radiation, x-rays.

It is recalled that the energy level 2 p is really triplet in character, *i.e.* 2 p_1, 2 p_2, and 2 p_3. Lines of the wave numbers 1 S − 2 p_1 and 1 S − 2 p_3, however, have never been photographed or observed visually for any element of this family. As mentioned in Chapter I, Sommerfeld has attempted to explain this fact by the use of "internal quantum numbers," consideration of which is beyond the scope of this book. We have never observed inelastic impact at voltages corresponding to 1 S − 2 p_1 or 1 S − 2 p_3. In magnesium the separation of this triplet, if it existed, could not be resolved by the methods employed for the measurement of resonance potentials, but such is not the case for some of the elements in this family, for example mercury, where the voltages should be 4.5, 4.9 and 5.4. Our measurements gave 4.9 alone. Accordingly in the present discussion we shall refer only to the 2 p_2 energy level. Recently Franck and Einsporn have obtained indirect evidence of the existence of these other potentials. If their work be accepted, some very interesting complications arise, both in theory and experiment, which are considered later. So far, the experimental evidence of all spectroscopy has shown that the 2 p_1 and 2 p_3 orbits are occupied only following the emission of a line of a subordinate series and a few combination lines, for example a transition of an electron from an *md* or an *ms* orbit. and that the 2 p_1 and 2 p_3 orbits do not represent the *initial state in any transition involving the emission of radiation.*

Returning to the discussion of magnesium, we find that two types of electronic impact between 4.33 and 7.61 volts may occur. The atom

may absorb 2.7 volts energy from the impacting electron, causing a displacement of a valence electron to the $2\,p_2$ orbit, with the subsequent emission of λ 4571. The impacting electron retains the remaining portion of its kinetic energy after rebound from the atom, suffering only the velocity loss of 2.7 volts. Secondly, the atom may absorb 4.33 volts energy from the impacting electron, causing a displacement of a valence electron to the $2\,P$ orbit. On referring to Figure 6 it is noted that but one energy level, $2\,p$, lies between the state $2\,P$ and the normal state $1\,S$. Transition from $2\,P$ to $2\,p$ involves zero change in the azimuthal quantum number and by the Bohr principle of selection should not take place. Hence the electron in the $2\,P$ orbit must return to normal by a single transition, resulting in the emission of $\nu = 1\,S - 2\,P$, λ 2852. Accordingly, on account of the two types of collision present, we should have between 4.33 and 7.61 volts a two-line spectrum consisting of the lines λ 4571 and λ 2852. This is shown in the second spectrogram of Figure 23, for a potential of 6.5 volts.

It is of interest to note that under the conditions of this experiment we have the most favorable opportunity for the production of $2\,p_2 - 2\,P$ if this line represented a physically possible interorbital transition. Only two transitions from $2\,P$ are mathematically possible, to $2\,p_2$ and to $1\,S$. The line $2\,p_2 - 2\,P$ would lie at λ 7587. Using dicyani stained plates having high sensitivity at this wave length, not a trace of the line could be detected, the two-line spectrum appearing alone. This constitutes a very interesting verification of the Bohr principle of selection.

Collision above 7.61 volts results in the complete ejection of a valence electron. The electron returns to the normal $1\,S$ orbit by successive interorbital transitions, each resulting in an emission of one quantum of some particular frequency ν_k subject to the condition laid down by Equation (73). An individual atom accordingly, in any single return to equilibrium following ionization, may emit only a few of the arc lines, in rare cases only the single convergence wave number $1\,S$, but with numerous atoms approaching equilibrium by the various different combinations of transitions possible, we have as the macroscopic result the emission of the complete arc spectrum. This is shown in the third spectrogram of Figure 23, obtained at 10 volts.

If an electron of 4.4 volts velocity, or greater, collides with an ionized magnesium atom, the single remaining valence electron may be ejected from the normal $1\,\mathfrak{S}$ state to the $2\,\mathfrak{P}$ state, as shown in Figure 7, the energy corresponding to 4.4 volts being abstracted from the impacting electron which rebounds from the atom with the equivalent velocity

loss. The atom in assuming its equilibrium state as a positive ion accordingly emits the pair $1\,\mathfrak{S} - 2\,\mathfrak{P}_{1,2}$, λ 2796 – 2802. This is the "single-line" spectrum of ionized magnesium, a doublet, analogous to the single-doublet spectra of the alkalis, considered later. It requires for its excitation the preliminary ionization of the atom for which a 7.61 volt collision is necessary. Hence it will appear only at potentials greater than 7.61 volts although the pair itself requires but 4.4 volts for its excitation. Two successive collisions are necessary, the first resulting in ionization of the normal atom, and the second corresponding to a resonance potential of the atom-ion. The pair appears clearly in the 10 volt spectrogram of Figure 23.

If an electron of 14.97 volts velocity, or greater, collides with an ionized magnesium atom, the single remaining valence electron may be completely ejected, leaving the atom doubly ionized. The electron returns to the normal $1\,\mathfrak{S}$ orbit of the simply ionized atom by successive interorbital transitions, each resulting in an emission of one quantum of some particular frequency ν_k subject to the condition laid down by Equation (75) where $V_i^* = 14.97$ volts. For many atoms, the composite result is the emission of all the enhanced or spark lines, the complete doublet spectrum of magnesium. This is shown by the last three spectrograms of Figure 23. Over thirty well known enhanced lines belonging to series are readily visible in the original negatives of these illustrations. The wave-lengths of some of the more prominent lines are indicated in the figure.

At 22.8 volts, corresponding to $1\,\mathfrak{S} + 1\,S$, there is a possibility of doubly ionizing magnesium in a single electronic collision. With any mechanical, symmetrical model of a heavy atom, it is rather difficult to see how this could occur, and as yet no one has shown that an increase in radiation takes place at this velocity. However, the numerical value is of importance in thermochemical relations as it gives the total work of double ionization regardless of how the process is effected.

At 46.9 volts and 1299 volts, respectively, the L and K x-radiations appear (cf. Chapter IX). Apparently no change in the visible radiation occurs as the voltage 46.9 is exceeded. One should expect to find the spectrum of doubly ionized magnesium in this voltage range. Possibly a difficulty in producing such spectra is the small probability of the three successive collisions necessary, where the energies absorbed from the impacting electrons have wide variation. In this case we require 7.61, 14.97 and a value slightly exceeding 46.9 volts, the excess arising in the fact that removal of two outer electrons produces some effect on the work required to eject an L-electron.

The foregoing discussion outlines the fundamental stages in the excitation of the spectra of magnesium by electronic impact. We have yet to consider certain auxiliary processes which involve absorption of radiation followed by electronic impact or processes which involve two successive electronic collisions, as mentioned on page 115, items (2) and (3).

If the current density is high, fundamental lines of the subordinate series may be excited below the ionization potential, in addition to the two-line spectrum. A valence electron of the normal atom is ejected to the 2 p_2 orbit by direct impact or more probably by absorption of radiation of wave number 1 S – 2 p_2 emitted by a neighboring atom which is previously excited. Before the first atom can assume equilibrium, with the resulting radiation 1 S – 2 p_2, it collides with an electron and the valence electron is displaced to a higher energy level, for example 1 s, 2 s, 3 d, etc. From these energy levels the electron may fall to 2 p_1, 2 p_2 or 2 p_3, giving rise to subordinate series triplets. Thus we have observed at 7 volts in addition to 1 S – 2 P and 1 S – 2 p_2 the following lines of subordinate series of magnesium.

Notation	λ
2 p_1 – 2 s	3336
2 p_1 – 3 d	3838
2 p_2 – 3 d	3832
2 p_3 – 3 d	3829
2 p_1 – 1 s	5183
2 p_2 – 1 s	5173
2 p_3 – 1 s	5168

For a similar reason we find lines of the subordinate series of the enhanced spectrum below 14.97 volts, the potential required to remove the second electron and produce double ionization. In the original negative for the 10 volt spectrogram[9] of Figure 23 the following enhanced lines of subordinate series are prominent in addition to the single-doublet spectrum 1 $\mathfrak{S}$ – 2 $\mathfrak{P}_{1,2}$.

Notation	λ
2 $\mathfrak{P}_1$ – 3 $\mathfrak{D}$	2798
2 $\mathfrak{P}_2$ – 3 $\mathfrak{D}$	2790
2 $\mathfrak{P}_1$ – 2 $\mathfrak{S}$	2936
2 $\mathfrak{P}_2$ – 2 $\mathfrak{S}$	2928

[9] See Phil. Mag., 42, 1006 (1921), Table I, for a complete analysis of these spectrograms.

The simply ionized atom absorbs radiation of wave number $1\,\mathfrak{S} - 2\,\mathfrak{P}_{1,2}$ and before it can assume equilibrium and emit this pair, it collides with an electron. The remaining valence electron is displaced to an outer orbit such as $2\,\mathfrak{S}$ or $3\,\mathfrak{D}$, in which states the ionized atom is capable of emitting the above listed lines.

This development of the spectrum of magnesium is typical of all the metals of this group of the periodic table. Franck and Hertz,[10] working with mercury vapor, were the first to obtain a single-line spectrum. Nearly every one who has made photographs at low voltage has since observed λ 2537 as a single line, the vapor frequently occurring as an impurity in spectra of other vapors, when not produced intentionally. We have observed the single-line and two-line spectrum of zinc as an impurity in magnesium.[11] McLennan and Henderson[12] show photographs of the single-line spectra of mercury, cadmium and zinc. They also in 1915 observed that the complete arc spectrum appeared slightly above the ionization potentials, the values of which were unknown at this date. McLennan and Ireton[13] show photographs of the two-line spectra of zinc and cadmium. No investigations of the enhanced spectra in the low voltage arc for metals of Group II, aside from magnesium, have been published, a problem upon which Dr. Meggers and the authors are engaged at the present time. However, the critical frequencies are fairly accurately known from spectroscopic data, except for mercury and radium. We are accordingly able to summarize completely in Table XX the successive stages of development in the spectra of these elements, excited by electronic impact. This table gives *all* the spectra arising in disturbances of the valence electrons, which the atom, in the absence of a magnetic or electric field, is capable of emitting.

Relation Between $1\,\mathfrak{S}$ and $1\,S$

There appears to be a definite relation of some physical significance between the limiting frequencies $1\,\mathfrak{S}$ and $1\,S$. In Table XXI are given the values of the ratio $1\,\mathfrak{S}\,/1\,S$, using the data of Table XX.

The physical significance of this ratio can be roughly obtained in the following manner. Referring to Table III, the magnesium atom is seen to consist of three shells of electrons in the arrangement 2, 8, 2. By means of an equation similar to (51) we shall compute the total

[10] Verh. Physik. Ges., 16, p. 512 (1914).
[11] Foote, Meggers and Mohler, Phil. Mag., 42, p. 1014 (1921).
[12] Proc. Roy. Soc., 91, pp. 485–91 (1915).
[13] Phil. Mag., 36, pp. 461–71 (1918).

TABLE XX

Development of Spectra of Metals of Group II by Electronic Impact

Element	Single-line Spectrum $1S - 2p_2$		Two-line Spectrum $1S - 2p_2$ and $1S - 2P$		Complete Arc Spectrum		Single-doublet Spark Spectrum $1\mathfrak{S} - 2\mathfrak{P}_{1,2}$		Complete Spark Spectrum	
	Determining Wave Number $1S - 2p_2$	Minimum Excitation Potential Volts	Determining Wave Number $1S - 2P$	Minimum Excitation Potential Volts	Determining Wave Number $1S$	Minimum Excitation Potential Volts	Determining Wave Number $1\mathfrak{S} - 2\mathfrak{P}_{1,2}$	Minimum* Excitation Potential Volts	Determining Wave Number $1\mathfrak{S}$	Minimum* Excitation Potential Volts
Mg......	21871	2.70	35051	4.33	61672	7.61	35761 35669	4.4	121267	14.97
Ca.......	15210	1.88	23652	2.92	49305	6.09	25414 25192	3.1	95740	11.82
Zn.......	32502	4.01	46745	5.77	75767	9.35	49355 48482	6.1 5.9	147544	18.21
Sr.......	14504	1.79	21698	2.68	45926	5.67	24517 23715	3.0 2.9	88952	10.98
Cd......	30656	3.78	43692	5.39	72539	8.95	46618 44136	5.8 5.4	140226	17.31
Ba......	12637	1.56	18060	2.23	42029	5.19	21952 20261	2.7 2.5	80665	9.96
Hg......	39413	4.86	54066	6.67	84178	10.39	?	?	16300(?)	20. ?
Ra......	12500?	1.5?	20700?	2.6?	40–45000?	5.0–5.5?	26209 21352	3.2 2.6	82862	10.23

* Atom must be first simply ionized requiring electronic collision with velocity loss shown in column 7.

energy of the outer ring (1) W_2 with both valence electrons and (2) W_1 with one valence electron.

$$W_r = -r\frac{Nhc}{n^2}\left(Z - p - q - s_r\right)^2, \tag{82}$$

$$W_2 = -2\frac{Nhc}{n^2}\left(12 - 2 - 8 - s_2\right)^2, \tag{83}$$

$$W_1 = -1\frac{Nhc}{n^2}\left(12 - 2 - 8 - s_1\right)^2 \cdot \tag{84}$$

The value W_2 represents the work required to remove both valence electrons and is accordingly proportional to $1\,\mathfrak{S} + 1\,S$. The value W_1 represents the work required to remove the second valence electron after the first has been ejected and is accordingly proportional to $1\,\mathfrak{S}$. Hence:

$$\frac{W_2}{W_1} = \frac{1\,\mathfrak{S} + 1\,S}{1\,\mathfrak{S}} = \frac{2(2 - 0.25)^2}{4} = 1.531, \quad \text{and}$$

$$\frac{1\,\mathfrak{S}}{1\,S} = 1.88. \tag{85}$$

This value agrees approximately with that given in Table XXI. Similar computations for the other elements lead to the same numerical relation. The value $1\,\mathfrak{S}$ for mercury in Table XX was obtained in this manner from the known magnitude of $1\,S$, since the series relations in the enhanced spectrum are unknown.

TABLE XXI

RATIO $1\,\mathfrak{S}/1\,S$ FOR METALS OF GROUP II

Element	$1\,\mathfrak{S}/1\,S$
Mg	1.97
Ca	1.94
Zn	1.95
Sr	1.94
Cd	1.93
Ba	1.92
	Mean 1.94

Metals of Group I of the Periodic Table

The metals of Group I as shown in Table X all have a single resonance potential. We accordingly find a three-stage development in the spectra. A single-line or more precisely a single-doublet spectrum, $1\ s - 2\ p_{1,2}$, appears at the resonance potential. The complete arc spectrum is excited at the ionization potential and at a still higher potential the enhanced spectrum appears.

There is no reason in the Bohr theory why resonance potentials of higher magnitudes, corresponding to $1\ s - 3\ p_{1,2}$, $1\ s - 4\ p_{1,2}$, etc., should not exist, a statement applying equally well to the metals of Group II. Thus we might expect that the valence electron could be displaced from the normal $1\ s$ orbit directly to any mp orbit as a result of inelastic collision with the proper energy exchange. In the complete arc spectrum the intensity of $1\ s - 2\ p$ is many times greater than that of $1\ s - 3\ p$. In fact in every series, the intensity of the lines, referred to absolute value from which plate- or eye-sensitivity is eliminated, decreases rapidly from the first term to zero at the convergence. Now it seems possible that just as the probability of the transfer of the valence electron from an mp orbit to the $1\ s$ orbit evidently decreases rapidly as m increases, so the probability of the displacement of the valence electron to an mp orbit as a result of electronic collision with a normal atom may decrease as m increases, even though all the impacting electrons have a velocity corresponding to $1\ s - mp$. If this were so, these higher resonance potentials might exist and not be detectable by the ordinary methods of measurement. For example if one hundred collisions resulting in a displacement of the valence electron to $2\ p$ occurred while one collision resulted in a displacement to the $3\ p$ orbit, the effect of the latter would be nearly indistinguishable by the electrical methods employed in the investigation of inelastic impact. On the other hand one collision of the $3\ p$ type in a hundred or more of the $2\ p$ type should produce an observable spectroscopic effect.

Referring to Figure 5, electronic displacements to the $3\ p$ orbit enable the vapor to emit $1\ s - 3\ p$, the second pair of the principal series, besides the first pair and infra-red lines representing the *indirect* transition from $3\ p$ to $2\ p$, and the first pair of each subordinate series. The various lines which may be emitted following a displacement to $3\ p_1$ are summarized in Table XVII. At the inelastic impact corresponding to $1\ s - 3\ p$ we should accordingly observe the emission of the following more important pairs: $1\ s - 2\ p$, $1\ s - 3\ p$, $2\ p - 2\ s$ and $2\ p - 3\ d$.

Foote and Meggers[14] attempted to investigate this for **caesium.** Unfortunately for this element the latter two pairs lie in the far infra-red and could not be observed. The wave number $1\,s - 2\,p_1$ corresponds to 1.4 volts; $1\,s - 3\,p_1$ to 2.7 volts; $1\,s - 4\,p_1$ to 3.2 volts; $1\,s - 5\,p_1$ to 3.4 volts; and $1\,s$ to 3.9 volts. The ratio of *absolute* intensities of the lines $(1\,s - 2\,p_1) \div (1\,s - 3\,p_1)$ *i.e.* λ 8521/λ 4555 were measured for a series of accelerating potentials as follows:

Volts	7	4	3.8	3.4	3.2	2.8
λ 8521/λ 4555	350	2100	8300	10500	>10000	$\doteq \infty$

Accordingly at voltages less than 3.9, the ionization potential, and greater than 2.7, corresponding to $1\,s - 3\,p$, there appears to be no emission of $1\,s - 3\,p_1$, λ 4555, which cannot be attributed to ionization. At 3.4 volts for example the intensity of $1\,s - 3\,p_1$ is but 1/10000 that of $1\,s - 2\,p_1$, although all the electrons have a velocity sufficient to eject the valence electron to the $3\,p_1$ orbit.

The electrons emitted by a heated cathode (equipotential surface) have a velocity distribution given by Maxwell's law. It may be readily shown that on account of this temperature distribution, the fractional number F of emitted electrons having a velocity greater by V_0 than the applied potential V is:

$$F = erf\,x + \frac{2\,x}{\sqrt{\pi}}\,e^{-x^2}, \quad \text{where } x^2 = 11600\;V_0/T\,, \qquad (86)$$

where T is the absolute temperature of the cathode. At a dull red heat about 30 electrons per 10,000 have a velocity 0.5 volt greater than V. One in 10,000 should be sufficient to account for the intensity of λ 4555 at 3.4 volts. Similar conclusions may be drawn from observations on other lines. For example the line $2\,p_1 - 5\,d$, λ 6974, was found by absolute intensity measurement to be of such low intensity below the ionization potential that its excitation may be explained by the small number of high velocity electrons present. No line, other than the pair $1\,s - 2\,p$, shows a rapid increase in intensity when the velocity of the electrons reaches that corresponding to its particular energy level. Hence we conclude that the valence electron may be ejected only to the $2\,p$ orbit, following electronic impact with the *normal* atom, thus confirming the data obtained by direct measurement of critical potentials.

[14] Bur. Standards Sci. Paper No. 386 (1920).

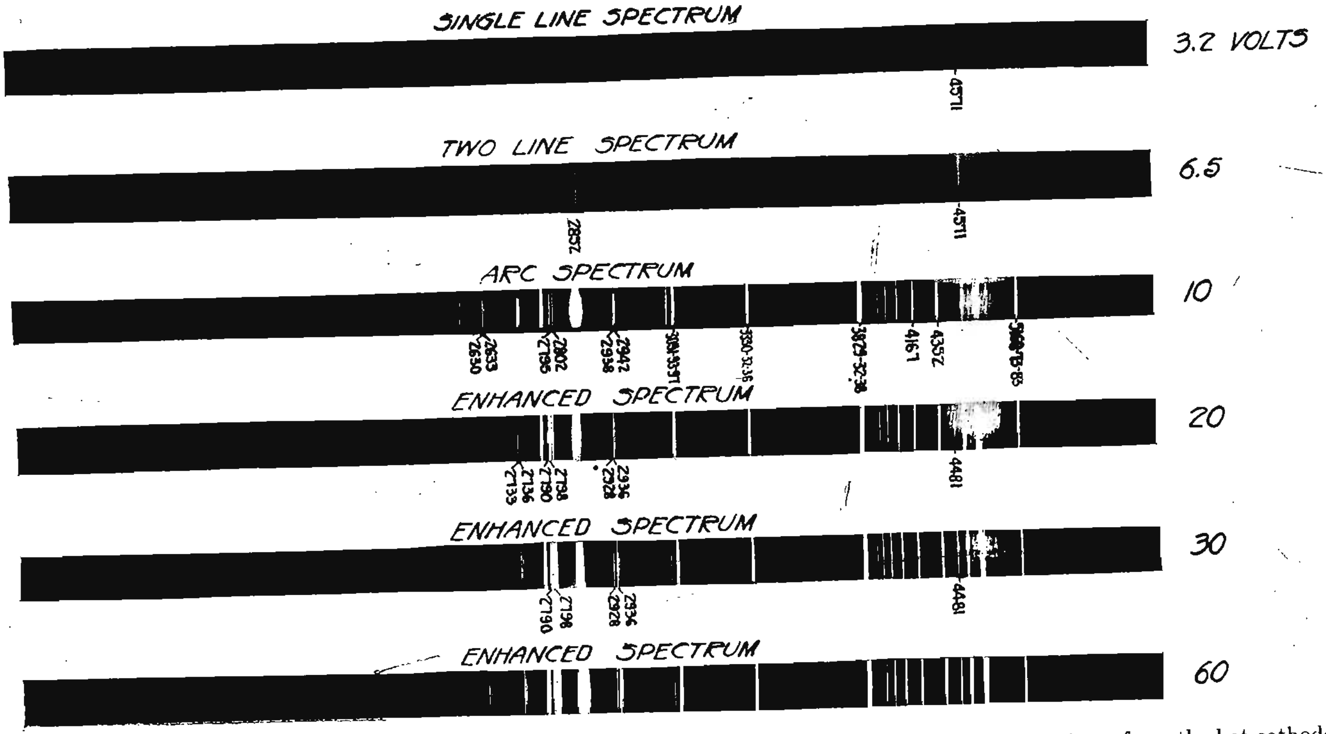


FIG. 23. Spectra of magnesium. The band of light around λ 4600 is fogging, due to the continuous spectrum from the hot cathode. Most of the fainter lines showing clearly in the negative are obscured in the process of reproduction. Between 200 and 300 lines are present at the higher voltages.

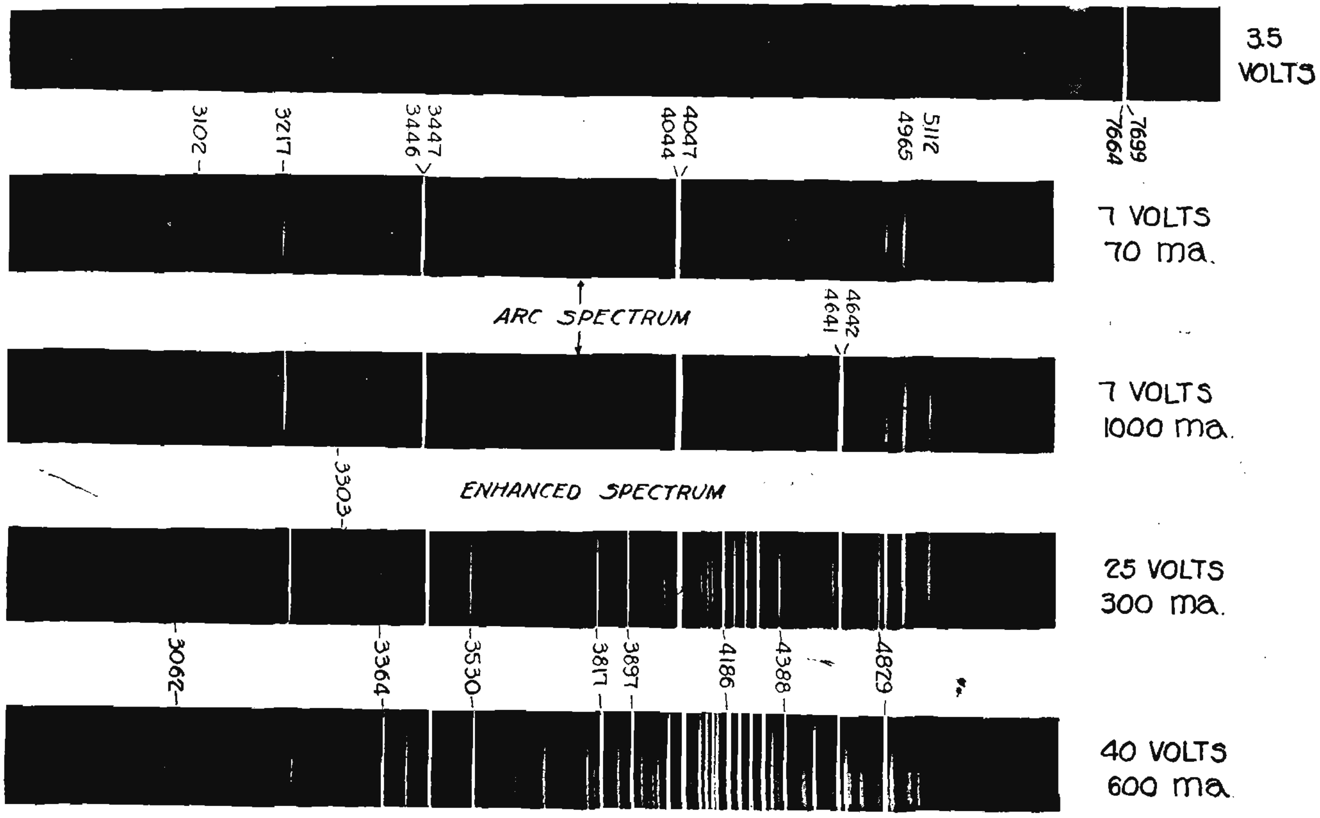


FIG. 24. Spectra of potassium. The upper spectrogram was made by the use of a dicyanin stained plate. The pair 1 s – is of course present at the higher voltages but was not recorded on the ordinary plates. The band of light in the red o upper spectrogram is due to fogging by the hot cathode.

As the electronic velocity is increased above that corresponding to the resonance potential, we have the emission of $1\,s - 2\,p$. As soon, however, as the ionization potential is reached all arc lines are emitted. If an atom emits any line of the principal series beyond $1\,s - 2\,p$, it cannot at the same time emit $1\,s - 2\,p$, as seen from Figure 5. Hence electrons, which just below the ionization potential give rise to $1\,s - 2\,p$, just above ionization produce other principal series lines at the sacrifice of $1\,s - 2\,p$. There should be accordingly, for the same current, a decrease in the intensity of $1\,s - 2\,p$, as the ionization potential is passed, a fact confirmed by direct experiment.

The intensity of each line above the ionization potential was observed to be approximately proportional to the number of electrons leaving the cathode. This follows from the quantum theory. The number of electronic collisions and hence, roughly, the number of quanta of any particular frequency is proportional to the number of electrons or approximately proportional to the total current, a fact substantiated earlier by Jolly and other investigators.

This work on caesium should be repeated, using a 3-electrode instead of 2-electrode discharge tube, and should be extended to other metals, especially mercury. The foregoing is by no means conclusive, for *quantitative* spectrophotographic measurements at and slightly above the threshold value of the plate are exceedingly difficult if not impossible.[15]

Foote and Meggers[16] show photographs of the single-doublet spectrum of caesium, λ 8521 and λ 8943 at the resonance potential, and the complete arc spectrum slightly above the ionization potential. The single-doublet emission spectra of the alkalis are precisely the absorption lines shown in Figure 15, the pair $1\,s - 2\,p_1$ and $1\,s - 2\,p_2$. The authors and Dr. Meggers,[17] using the design of Figure 22, have obtained photographs illustrating the successive stage development in the spectra of sodium and potassium, the latter being reproduced here as Figure 24.

With potassium, from 1.60 to 4.32 volts, we have the single pair λ 7664 and λ 7699, as seen in the first spectrogram. From 4.32 to about 20 volts the arc spectrum consisting of the series of doublets represented by Equations (34) to (37) are excited, as seen in the second and third spectrograms. Above about 20 volts the enhanced lines are prominent,

[15] Dr. C. E. Kenneth Mees, Director, Eastman Kodak Research Laboratory, where every conceivable means and instrument for spectrophotographic analysis are at hand, together with a staff trained in the technique of plate sensitometry, in 1920 stated that it was a fixed policy of their laboratory not to rely on spectrophotographic photometry for such types of problem, if other methods are possible. It is certainly doubtful if any laboratory not specially equipped for such work can hope to secure unquestionable results.

[16] *Loc. cit.*

[17] Foote, Meggers and Mohler, Astrophys. J., 55, pp. 145–61 (1922).

appearing in the last two spectrograms. Several hundred lines are readily visible on the original negatives.

The third spectrogram shows the pair 1 *s* — 3 *d*, which as mentioned on page 36 is an exception to the principle of selection, since the change in azimuthal quantum number is two units. Here the presence of the line cannot be attributed to an incipient Stark effect, since there is no applied field in the space between the grid and plate of Figure 22. The corresponding pair in sodium is similarly excited. These exceptional lines appear at high current density, and the physical basis for their excitation is still an open question.[18]

With sodium, from 2.09 to 5.12 volts we have the single-pair, the D-lines. From 5.12 to about 35 volts the complete arc spectrum appears, while above 35 volts the many-line enhanced spectrum is excited.

The enhanced spectra of the alkalis should resemble the arc spectra of the rare gases. In the richness and complexity of the lines the resemblance fulfils all expectations. As yet, however, no series relations have been determined. It is nevertheless possible to roughly estimate, theoretically, the potentials required to excite these enhanced lines. Referring to Table III, for sodium, we have the *K*-ring with 2 electrons, the *L*-ring with 8 electrons and the outer ring with the single valence electron. Suppose the valence electron is removed by a 5.1 volt electronic impact and then an electron is removed from the *L*-orbit, thus leaving the atom doubly ionized. The atom is now ready to emit any line of the enhanced spectrum. Suppose that the highest convergence frequency in the enhanced spectrum is emitted. Would this involve the return of an electron from without the atom to the *L*-ring from which it was originally ejected? There is some reason for believing that the electron should assume an orbit outside the shell of seven, forming a metastable sodium ion. That is, two kinds of simply ionized sodium atoms may exist with electrons distributed in shells as follows:

1st	2d	3d Shell
2	8	
2	7	1

The first type is in a state preliminary to the emission of the arc spectrum; the second type is in the normal state for the absorption of principal

[18] Possibly it has something to do with the interaction of atomic fields of neighboring atoms and ions. This suggestion was made by the authors, Phil. Mag., 43, pp. 659–61 (1922), and later was affirmed by Bohr, Phil. Mag., 43, pp. 1112–16 (1922), in discussion of the paper.

series enhanced lines, a state corresponding to 1 $\mathfrak{S}$ of the ionized alkali earths. In the second arrangement, the single outside electron revolves in a quantized orbit of unit azimuthal quantum number, about the nucleus and the nine remaining electrons.

Proceeding by a method identical with that used in the derivation of the Ritz equation, page 32, we shall compute the energy required to eject the outer electron in the configuration 2: 7: 1.

Let p = number of electrons in inner ring, radius a_1
q = " " " " 2d " radius a_2

atomic no. = $Z = p + q + k$ where $k = 2$ for spark spectra and 1 for arc spectra.

$$E_P + T = -\frac{ke^2}{r} + \frac{c_1}{r^3} + \frac{1}{2\,m}\left(p_r^2 + \frac{1}{r^2}\frac{n^2h^2}{4\,\pi^2}\right) = W, \tag{87}$$

where
$$c_1 = \frac{e^2}{4}\,(pa_1^4 + qa_2^4). \tag{88}$$

Performing the quantum integration as in Equations (28) and (29) we obtain:

$$W = -\frac{Nhck^2}{(n_a + n_r + a)^2}, \tag{89}$$

where
$$a = \frac{(2\,\pi)^4\,m^2e^2kc_1}{n_a^3h^4}. \tag{90}$$

For the normal state $n_a + n_r = 1$, and expressing our values in volts, we find from Equation (89):

$$\text{Normal state} \qquad V = \frac{13.55\,k^2}{(1 + a)^2}. \tag{91}$$

Eliminating a_1 and a_2 from Equation (88) by use of Equations (47) to (49) we obtain from Equation (90) when $n_a + n_r = 1$

$$a = \frac{k}{4}\left[\frac{p}{(Z - s_p)^2} + \frac{16\,q}{(Z - p - s_q)^2}\right]. \tag{92}$$

On account of the assumptions involved in the derivation of Equation (92), coplanar orbits, etc., it should not be expected that it would yield exact numerical magnitudes. But by applying Equations (91) and (92), first to arc spectra and then to spark spectra, the ratios a^*/a and V^*/V *may* possess some physical significance. Substituting the value of V, the simple ionization potential, in Equation (91) and solving for a where $k = 1$, we may compute a^* from the ratio a^*/a obtained through Equation (92), and then by Equation (91) compute V^*

where $k = 2$. We thus obtain the value of the work, expressed in volts, necessary to remove the second electron from its quantized orbit in the simply ionized sodium atom. The equations are equally applicable to the other alkalis. We accordingly compute the following table:

Element	a^*/a	V^*
Na	1.50	14
K	1.50	11
Rb	1.66	10
Cs	1.68	9

These voltages should correspond approximately to the highest convergence frequencies of the spark spectra.

In the case of sodium, for example, the complete spark spectrum requires for its excitation the removal of one L-electron corresponding to the work $La = 35$ volts, as shown in Chapter IX, followed by a 14 volt collision through which the outer electron is removed. The total work required to remove both electrons is equivalent to the sum of these voltages or 49 volts. The process may be effected in the reverse order; removal of the valence electron requiring 5 volts followed by removal of the L-electron at 44 volts, the sum necessarily being the same. The enhanced spectrum should accordingly begin to appear in an arc at about 35 volts. Now by three successive impacts resulting in (1) ejection of valence electron, (2) transition of L-electron to new quantized orbit, (3) ejection of the electron from this new orbit, the enhanced spectrum might appear at a somewhat lower voltage. However, since three successive impacts are in general improbable, we may conclude that the enhanced spectrum of sodium accompanies its L-radiation, at the minimum voltage corresponding to $La = 35$. This conclusion is substantiated by the work of Dr. Meggers and the authors.

In a similar manner, the enhanced spectrum of potassium should accompany its M-radiation appearing at the minimum voltage Ma. As shown in Chapter IX, $Ma = 20$ to 23 volts.[19] We see in Figure 24 that the enhanced lines have put in their appearance at 25 volts, confirming the above deductions.

Likewise, the enhanced spectra of rubidium and caesium should accompany their N and O x-radiation respectively. No data exist relative to either these x-rays or the excitation potentials for the enhanced spectra.

[19] $Ma_{1,2} = 20$. When the limits are complex, probably the lower value is effective.

We may contrast the behavior of the alkalis and the alkali earths. Simple ionization of the latter leaves the atom in a normal state for the absorption of enhanced lines, in a state where the remaining valence electron occupies the 1 $\mathfrak{S}$ orbit. Simple ionization of the alkali, however, does not do this. As a consequence the entire enhanced spectrum of an alkali earth appears at the potential V^* corresponding to 1 $\mathfrak{S}$, whereas it requires a potential somewhat greater than V^* to excite the enhanced spectrum of an alkali. For example, in sodium, although $V^* = 14$ volts, the enhanced lines do not appear below $La = 35$ volts. Similarly with potassium: although $V^* = 11$ volts, it requires 20 volt electronic impact to produce the enhanced lines.

Table XXII summarizes the development in the spectra of metals of Group I, excited by electronic discharge.

The Rare Gases

The spectra of the rare gases, except ionized helium, are characterized by exceedingly complicated combination systems of series lines. Most of the fundamentally important lines should lie far in the ultraviolet, in many cases beyond the range of the vacuum spectrograph.

Helium.—As seen from Table XIV helium has an ionization potential about 25.5 volts and two resonance potentials at 20.4 and 21.2 volts. If we could reason by analogy to the alkali earths, we should expect a single line spectrum, λ 603, at 20.4 volts and a two-line spectrum, λ 603 and λ 580 at 21.2 volts. However, as discussed in the section on "The Normal Helium Atom," Chapter III, only the line 585 is known, and the true significance of and nomenclature for this line is possibly a matter of doubt. We are accordingly unable to draw any conclusion in regard to the excitation of helium lines below the ionization potential.[20]

The work of double ionization of Bohr's normal *coplanar* helium atom should be 83 volts, as shown by Equation (65). We have seen that this configuration is incorrect, since it gives 28.8 instead of 25.5 for the ionization potential. We may, however, readily determine the work required to remove the second electron after the first has been ejected. This value, computed from Equation (20) by putting $Z = 2$, is 54.2 volts. Hence the correct value for the work of double ionization is 54.2 + 25.5 or 79.7 volts.[21]

[20] Franck and Knipping's work, as discussed on page 73, indicates the presence of $1S - 2P$ and $1S - 3P$ below ionization. See also important foot note 39, page 77, added since book was in page proof.

[21] Possibly 79.5 is a closer value.

TABLE XXII

DEVELOPMENT OF SPECTRA OF METALS OF GROUP I BY ELECTRONIC IMPACT

Element	Single-Doublet Spectrum			Complete Arc Spectrum		Complete Spark Spectrum		
	Wave Number		Minimum Excitation Potential Volts	Determining Wave Number 1 s	Minimum Excitation Potential Volts	Determining Wave Number Notation	Minimum Excitation Potential Volts	Highest Convergence Frequency Expressed in Volts*
	$1s - 2p_1$	$1s - 2p_2$						
Li.	14903.8	14903.5	1.84	43486	5.37	$K\alpha$	62	—
Na.	16973	16956	2.10	41449	5.12	$L\alpha_{1,2}$	35	14
K.	13043	12985	1.61	35006	4.32	$M\alpha_{1,2}$	20	11
Cu.	30784	30535	3.80	62308	7.69	$M\alpha_{1,2}$**	100?	—
Rb.	12817	12579	1.58	33689	4.16	$N\alpha$	?	10
Ag.	30473	29552	3.76	61096	7.54	$N\alpha_3$**	85?	—
Cs.	11732	11178	1.45	31405	3.88	$O\alpha$	—	9
Au.	41174	37359	5.1	70000?	8 to 9?	$O\alpha$	—	—

* See table, page 132.

** The potentials $M\alpha_{1,2}$ are the values indicated in Figs. 33 and 35. There are reasons both theoretical and experimental for believing that softer x-ray limits may appear both in copper and silver. The enhanced lines undoubtedly can be excited at lower voltages than the limits indicated. Since copper, for example, may have the valence 2, the second valence electron, which originally belongs to an x-ray orbit and which is probably responsible for spark spectra, must be fairly loosely bound.

Accordingly, the arc lines represented by Figure 10 should appear at a potential of 25.5 volts. Spark lines should be excited at 54.2 volts in case the impacting electron collides with a simply ionized atom. A 79.7 volt electron is capable of doubly ionizing the normal atom so that an increase in intensity of the spark lines may take place at this voltage.

We have seen from Figure 2 that the wave-lengths and even the fine structure of the spark lines are accurately given by Equation (22). The mean wave-length of each spark line is fairly closely represented by the simpler Equation (9′) in which the higher order terms of Equation (22) are omitted:

$$\nu = 4\,N_{\text{He}}\left(\frac{1}{n^2} - \frac{1}{m^2}\right). \qquad (9')$$

Table XXIII gives the computed wave-lengths for the first and second terms and convergence of each of the four series where $n = 1, 2, 3, 4$ respectively. In a general way the first series corresponds to the

TABLE XXIII

IMPORTANT ENHANCED LINES OF HELIUM

Line	$4\,N_{\text{He}}\left(\frac{1}{1^2}-\frac{1}{m^2}\right)$		$4\,N_{\text{He}}\left(\frac{1}{2^2}-\frac{1}{m^2}\right)$		$4\,N_{\text{He}}\left(\frac{1}{3^2}-\frac{1}{m^2}\right)$		$4\,N_{\text{He}}\left(\frac{1}{4^2}-\frac{1}{m^2}\right)$	
	m	$\lambda(vac)$	m	$\lambda(vac)$	m	$\lambda(air)$	m	$\lambda(air)$
First.	2	304 A	3	1640 A	4	4686 A	5	10124 A
Second.	3	256	4	1215	5	3203	6	6560
Convergence.	∞	228	∞	911	∞	2050	∞	3644
Corresponding series in hydrogen	Lyman		Balmer		Paschen		Brackett*	

* Cf. Nature, 109, p. 209 (1922).

principal doublet enhanced series of the alkali earths and the second series to the subordinate doublet series of these metals, while the direct observations on the excitation potential for the enhanced lines of helium are confined to the line λ 4686 of the third series. We may be certain, however, if the latter appears, the lines of the more important series are also present in even greater intensity.

Compton and Lilly,[22] using a two electrode discharge tube, observed the emission of the arc lines of helium, Figure 10, at an applied potential of 25 to 35 volts. The spark line λ 4686, in an intense arc, was observed

[22] Astrophys. J., 52, pp. 1–7 (1920).

at a minimum potential of 55 volts, and the brightness of the line increased considerably at 80 volts. At low gas pressure and current density λ 4686 was not perceptibly excited below 80 volts. Under these conditions two successive collisions, each resulting in the expulsion of a single electron, were much less probable than a single 80 volt collision resulting in the ejection of two electrons.

We may accordingly conclude that, as predicted by theory, the arc spectrum of helium appears at 25.5 volts, the ionization potential, and that the spark lines are excited at 54.2, by successive impact, and at 79.7 by single impact, the latter values corresponding respectively to the work required to eject the second electron after the first is removed, and to the work required to eject both electrons.

Neon.—The intricate spectrum of neon has been recently correlated in series by Paschen.[23] It is characterized by sequences of the form $1\ s_x - mp_y$, which are analogous to the principal series of the metals, and sequences of the form $2\ p_x - md_y$ and $2\ p_x - ms_y$, which are analogous to the subordinate series of the metals. As shown in Table XIV there are two resonance potentials and three ionization potentials. The latter all correspond to the removal of a single electron as none is great enough to represent successive or double ionization. Apparently there are three slightly different energy levels in which the outer shell of eight electrons are distributed. The work required to remove a second electron from the neon atom after the first has been ejected cannot be computed nor has it been observed experimentally.

Horton and Davies[24] have observed visually the stage development in the neon spectrum at the three ionization potentials. Their conclusions are summarized as follows.

First ionization 16.7 volts.	No visible radiation. Probably all the radiation lies in the extreme ultra-violet.
Second ionization 20.0 volts.	Principal series lines $1\ s_x - mp_y$ begin to appear.
Third ionization 22.8 volts.	Subordinate series lines $2\ p_x - ms_y$ and $2\ p_x - md_y$ begin to appear.

Apparently the phenomena concerned with the production of the arc lines of neon are nearly as complicated as the spectrum itself. The series relations in the arc spectrum may be intimately connected with those in the L series of the x-radiation.[25] Higher types of spectra which are probably enhanced lines may be obtained in a spark discharge but

[23] Ann. Physik, 60, p. 405 (1919); 63, p. 201 (1920). This work is simply summarized by Fowler, "Series in Line Spectra," Chapter XXI.

[24] Phil. Mag., 41, pp. 921–40 (1921).

[25] Grotrian, Z. Physik, 8, p. 116 (1921), pointed out that a constant frequency difference between arc series is apparently equal to the extrapolated L-doublet separations.

no attempts have been made to relate these to the velocity loss at electronic impact.

Franck and Einsporn's Observations on Mercury

In order to discuss the recent paper of Franck and Einsporn[26] with sufficient clarity, it appeared advisable to consider it following the foregoing sections, rather than to have introduced it earlier in the treatment of the metals of Group II. These investigators obtained evidence that there are a large number of resonance potentials in mercury vapor and that lines which have never been observed should be present in considerable intensity.

The method[27] employed is a common one in the determination of critical potentials (see general references to Chapter III). The electrons from a hot wire fall through a definite potential and collide with mercury atoms. The radiation, emitted by an atom in returning to or toward the normal state following the disturbance produced by an inelastic impact, is measured by its photo-electric effect upon an auxiliary electrode. The photo-electric current leaving this electrode is plotted as a function of the accelerating voltage of the impacting electrons. As the velocity, or equivalent voltage, of the latter is gradually increased, an increase in the radiation, and hence in the observed photo-electric current, takes place at each critical voltage representing an inelastic impact. Ordinarily one observes an increase at 4.9 and 6.7 volts corresponding to the well-known resonance potentials, an increase at 10.3 corresponding to ionization, and further increases at combinations of these values such as $4.9 + 4.9 = 9.8$; $4.9 + 6.7 = 11.6$, etc. These latter represent successive collisions of the impacting electrons.

Franck and Einsporn's curves, which were obtained with the greatest precision, show these, and many more, rapid increases, as illustrated by Figure 25. In Table 24 is their interpretation of the observed critical voltages. Column 2 gives the observed voltages obtained from Figure 25 and similar curves; column 6 the series notation of the radiation supposedly producing the effects observed; and the last column gives the values computed from the wave numbers by Equation (63). Point No. 3 at 5.32 volts corresponds closely to measurements of McLennan and Edwards,[28] who found a group of absorption bands in mercury

[26] Z. Physik, 2, pp. 18–29 (1920).

[27] This method, which permits of many modifications, was devised by Davis and Goucher, Phys. R. 10, p. 101 (1917), and has proved to be one of the most important means for the study of electron impact.

[28] Phil. Mag., 30, pp. 695–700 (1915).

vapor between λ 2313 and λ 2338. These have been since observed as emission bands by Grotrian.[29] Probably they have no relation to the arc spectrum of the atom.

Point 13 corresponds to a displacement of the valence electron to the 3 p_2 orbit and point 14 to a displacement to either 3 P or 3 d'. Points

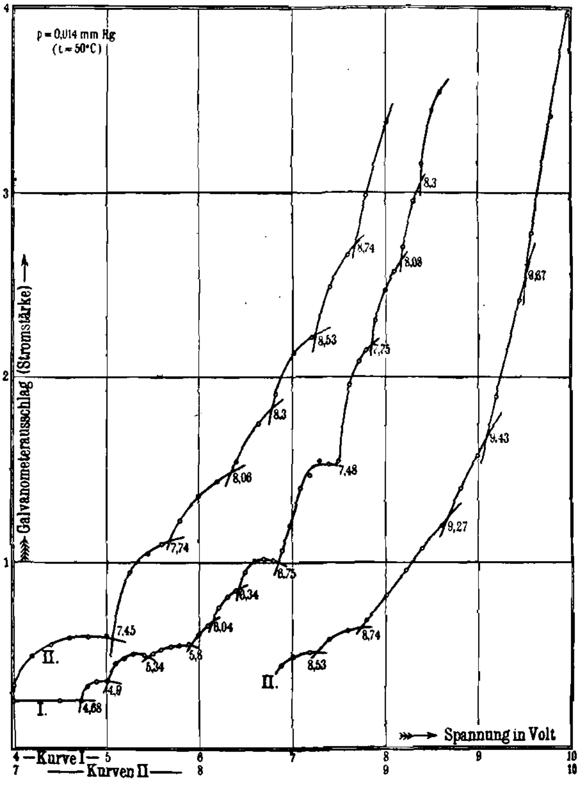


FIG. 25. Photo-electric current versus accelerating voltage. Franck and Einsporn's observations with mercury vapor.

16 and 17 may be due to displacements to higher energy levels or may be the result of two successive collisions, each displacing an electron to a 2 p orbit. Besides these ejections to the higher mp_2 and mP orbits we note displacements to 2 p_3 in points 1, 15 and possibly 16, and to 2 p_1 in point 4. Point 5 corresponds to the removal of an electron from the 2 p_3 orbit, an effect of cumulative ionization (Chapter VI).

[29] Z. Physik, 5, pp. 148–58 (1921).

TABLE XXIV

CRITICAL VOLTAGES IN MERCURY VAPOR; FRANCK AND EINSPORN

No.	Observed Volts	Intensity of Radiation	λ	ν	Notation	Computed Volts
1	4.68	Strong.	2656	37643	$1S - 2p_3$	4.66
2	4.9	Very strong, especially at high pressure.	2537	39413	$1S - 2p_2$	4.86
3	5.32	Weak.	2313 to 2338		?	5.3
4	5.47	Weak; at medium pressure strong.	2271	44041	$1S - 2p_1$	5.43
5	5.76	Strong.	2150	46534	$2p_3$	5.73
6	6.04	Weak.	?	?	?	?
7	6.30	Weak.	?	?	?	?
8	6.73	Medium strong.	1849	54066	$1S - 2P$	6.67
9	7.12	Strong at high pressure; weak at low pressure.	?	?	?	?
10	7.46	Medium strong.	?	?	?	?
11	7.73	Medium strong.	1604	62347	$1S - 1s$	7.69
12	8.35	Weak.	?	?	?	?
13	8.64	Weak.	1436	69658	$1S - 3p_2$	8.58
14	8.86	Medium strong.	1403 1400	71291 71393	$1S - 3P$ $1S - 3d'$	8.79 8.81
15	9.37	Weak.	2656 + 2656	37643	$1S - 2p_3$	4.66 + 4.6 = 9.3
16	9.60	Weak.	1308 { 2556 +2537	76463 37643 39413	$1S - 4p_2$ $1S - 2p_3$ $1S - 2p_2$	9.44 4.66 + 4.8 = 9.5
17	9.79	Medium strong.	{ 2537 +2537 1269	39413 78810	$1S - 2p_2$ $1S - 2p_2$ $1S - 4P$	4.86 + 4.8 = 9.7 9.73
18	10.38	Strong at low pressure; weak at high pressure.	1188	84178	$1S$	10.39

There is nothing contradictory to the quantum theory in the presence of inelastic impacts corresponding to $1\ S - 2\ p_1$ and $1\ S - 2\ p_3$ or to the other higher *mp* and *mP* terms. Displacement *by electronic impact* to $2\ p_1$ or $2\ p_3$ does not violate the principle of selection even when applied to so restricted a theory as that involved by Sommerfeld's internal quantum numbers,[30] since no radiation is absorbed or emitted. However, these inelastic collisions were observed through the effect of the resulting radiation. Moreover, if an electron is displaced to $2\ p_3$, the next orbit to $1\ S$, the only radiation which can be emitted directly would appear to be $1\ S - 2\ p_3$. Figure 25 shows that the *increase* in photo-electric current, which is proportional to the intensity of radiation, is just as great as $1\ S - 2\ p_3$ (4.68 volts) as at $1\ S - 2\ p_2$ (4.9 volts). Hence this unknown line λ 2656 should have been as bright as the well-known line λ 2537. It is scarcely possible that if such a line existed it would not have been observed in the arc spectrum of mercury, which has been investigated with almost all possible electron velocities in this neighborhood. A similar statement applies to the emission of $1\ S - 2\ p_1$, λ 2271. Possibly the inelastic impacts corresponding to these lines exist and a secondary process such as interatomic collision produces a transfer from $2\ p_1$ or $2\ p_3$ to $2\ p_2$, so that the resulting radiation is $1\ S - 2\ p_2$. Or ejection of a valence electron to $2\ p_1$ and $2\ p_3$ may give rise to a metastable form of the atom which, as discussed on page 106, possesses an electron affinity. Molecules may be then formed and the increase in the photo-electric current may be due to the decomposition of these metastable compounds of excited and normal atoms.

The subject is by no means closed. If further work more clearly interprets and verifies the present observations, it will not seriously conflict with the principles developed in this book. In the discussion of resonance potentials where we have made the statement "only two resonance potentials exist" we may eventually modify this to read "only two important or pronounced resonance potentials exist," admitting the possibility of a relatively small number of displacements to higher energy levels. Possibly some one will be able to demonstrate that lines involving higher series terms are emitted as a result of electronic impact below the ionization potential, all other effects of cumulative ionization being subordinated. At the present time, however, cumulative ionization and the few high velocity electrons always present on account of velocity distribution are easily sufficient to explain all experiments where higher series terms have been observed spectroscopically below the ionization potential.

[30] Sommerfeld, "Atombau," 3d Ed., Chapter VI, Section 5.

Quantitative Spectroscopic Analysis in its Relation to the Origin of Spectra

The possibility of making quantitative analyses by spectroscopic means has been agitated for a century. Some success has been attained in the past, but many of the excellent ideas proposed by such pioneers in this field as Lockyer,[31] Hartley[32] and more recently by de Gramont[33] have not received the attention they merit. For several years Dr. W. F. Meggers and his colleagues have been engaged in a systematic investigation of the possibilities of the method and have clearly demonstrated that quantitative analyses can be made, at least when the material sought occurs in small percentages, of the order of one per cent and less.[34]

Several experimental facts have been disclosed in this work which have some bearing upon the subject matter of this book. These will be considered in detail in a future paper by Dr. Meggers, who has placed the preliminary draft of his manuscript at our disposal. The empirically developed subject of spectroscopic analysis has to deal with two general phenomena: (1) the "long lines" of Lockyer, and (2) the "raies ultimes" of de Gramont or "persistent" lines of Hartley. As to the application of these phenomena to precise analysis, the original papers of Meggers must be consulted.

Long Lines. — If the entire spark or arc discharge is focused on the slit of a spectroscope so that the poles appear in the spectrum, certain lines of an impurity, or element occurring in a small proportion, appear long, extending from pole to pole, while the emission of other spectral lines is confined to a short distance in the immediate neighborhood of the poles. With increasing percentage of impurity the short lines increase in length.

Raies Ultimes. — As the percentage of the impurity is decreased, more and more of its spectral lines disappear. Certain lines, however, persist even when the impurity, magnesium for example, is present in the extremely minute extent of one part in 10^{10}. The persistent lines, termed by de Gramont, "raies ultimes," were recognized as not being necessarily the strong or intense lines of the ordinary spectrum. Furthermore the type of persistent line depends upon the method of excitation.

In general the sensitive lines for any element are both "long lines" and "raies ultimes." Discrepancies arise here and there which are

[31] Phil. Trans. 163, pp. 253, 639 (1873).
[32] Phil. Trans. 175, p. 325 (1884).
[33] Ann. chim. phys. 17, pp. 437–77 (1909). Compt. rend., 171, p. 1106 (1920).
[34] Meggers, Kiess and Stimson, Bur. Standards Sci. Paper No. 444.

probably attributable to the fact that different observers have investigated different spectral regions and certain lines have been thought to have been the long lines when the actual long lines may lie in a spectral region not yet investigated carefully.

Table XXV summarizes Dr. Megger's correlation of the raies ultimes made from empirical spectroscopic observations. It may be found, especially with elements of other than Groups I and II of the periodic table, that as the spectral range investigated is extended, even *more* sensitive lines will be discovered replacing some of those here listed.

TABLE XXV

RAIES ULTIMES OF THE ELEMENTS

Element	Wave-length Angstrom Units	Intensity		Notation
		Arc	Spark	
Li	6707.85 6708.00	20	20	$1s - 2p_1$ $1s - 2p_2$
	4602.19	10	8	$2p - 4d$
Na	5889.96	50	20	$1s - 2p_1$
	5895.93	35	15	$1s - 2p_2$
	3302.35	30	20	$1s - 3p_1$
K	7664.94	40	30	$1s - 2p_1$
	7669.01	30	20	$1s - 2p_2$
	4044.15	30	20	$1s - 3p_1$
Rb	4201.82	30	20	$1s - 3p_1$
	4215.56	20	10	$1s - 3p_2$
Cs	4555.3	20	10	$1s - 3p_1$
	4593.2	10	5	$1s - 3p_2$
Cu	3247.53	100	30	$1s - 2p_1$
Ag	3280.66	100	30	$1s - 2p_1$
Au	2427.97	10	20	$1s - 2p_1$
Mg	2852.13	100	20	$1S - 2P$
	2795.53	20	50	$1\mathfrak{S} - 2\mathfrak{P}_1$
Ca	4226.72	100	10	$1S - 2P$
	3933.67	50	100	$1\mathfrak{S} - 2\mathfrak{P}_1$
Sr	4607.34	50	20	$1S - 2P$
	4077.75	20	40	$1\mathfrak{S} - 2\mathfrak{P}_1$
Ba	5535.53	10	10	$1S - 2P$
	4554.04	10	20	$1\mathfrak{S} - 2\mathfrak{P}_1$
Zn	3075.88	8	5	$1S - 2p_2$
	2138.5	4	4	$1S - 2P$
d	3261.05	20	6	$1S - 2p_2$
	2288.03	10	10	$1S - 2P$
	2144.39	4	8	$1\mathfrak{S} - 2\mathfrak{P}_1$

TABLE XXV — *Continued*

RAIES ULTIMES OF THE ELEMENTS

Element	Wave-length Angstrom Units	Intensity		Notation
		Arc	Spark	
Hg	2536.52	10	10	$1S - 2p_2$
Sc	3630.75	15	50	
Yt	3710.29	30	100	
Al	3961.54	100	20	$2p_1 - 1s$
Ga	4172.05	30	20	$2p_1 - 1s$
In	4511.37	100	20	$2p_1 - 1s$
Tl	5350.49	100	30	$2p_1 - 1s$
C	2478.6	10	10	
Si	2881.59	30	15	
Ti	3361.22	10	30	
Zr	3391.98	10	20	
Ge	3039.08	50	20	
Sn	2863.32 3262.31	20 100	15 30	
Pb	4057.84	100	50	
V	4379.24	30	30	
Cb	4058.97	50	10	
Ta	3311.13	10	3	
P	2535.63 2553.32		5 5	
As	2349.84 2780.24	10 10	10 10	

TABLE XXV — *Continued*

RAIES ULTIMES OF THE ELEMENTS

Element	Wave-length Angstrom Units	Intensity		Notation
		Arc	Spark	
Sb.	2528.54	10	20	
Bi.	3067.69	100	30	
Cr.	3578.68	30	20	
	3593.48	30	20	
	4254.34	50	50	
Mo.	3798.25	50	20	
	3864.11	50	20	
W.	4008.77	10	10	
Te.	2385.81	3	20	
Mn.	2576.15	4	30	
	4030.80	100	20	
Fe.	2382.04	6	10	
	2749.33	4	20	
	3734.86	5	10	
Co.	2388.93	2	10	
Ni.	2416.15	2	15	
Ru.	3498.95	50	8	
Rh.	3434.90	100	10	
Pd.	3609.55	100	50	
Ir.	3220.79	15	5	
Pt.	3922.96	10	15	

The important fact which Meggers points out is that these ra ultimes are almost always prominent absorption lines, and are in m

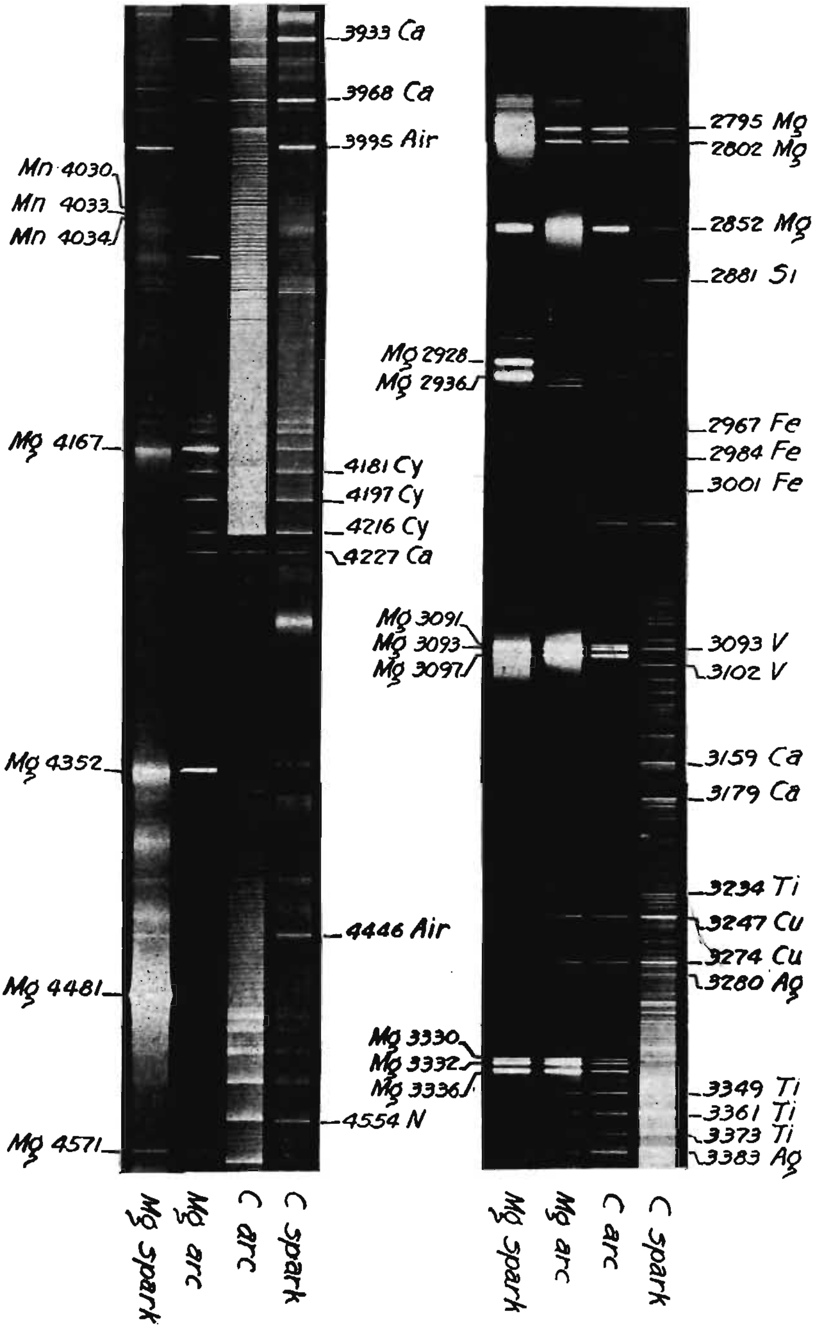


FIG. 26. "Raies ultimes" for several elements.

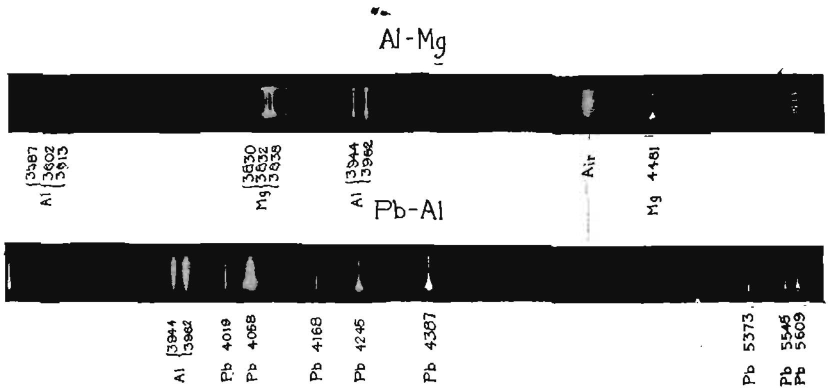


FIG. 27. An example of "long" and "short" lines.

cases the *first lines* of series converging at 1 *S* or 1*s*, where the spectrum of the element concerned has been correlated in series.

That is, they are the same lines which determine the value of the resonance potential, or which appear in the so-called single-line spectrum of the element excited below the ionization potential. We accordingly have another method for locating these fundamentally important lines of elements for which the series relations have not been as yet established.

If the spectra are excited in the arc the raie ultime is usually the first line of a fundamentally important arc series; if in a condensed spark, usually the first line of a fundamentally important spark series. This fact is indicated by the intensity relations given in Table XXV.

Figure 26 clearly illustrates these conclusions. The material investigated was carbon, which contained small amounts of a large number of impurities for several of which the series relations are known. The outer spectrogram in each group was obtained with a spark discharge. The magnesium lines appearing are the pair λ 2795 – 2802, 1 $\mathfrak{S}$ – 2 $\mathfrak{P}$ belonging to the spark spectrum and the single line λ 2852, 1 *S* – 2 *P*, of the arc spectrum, the former being present in the greater intensity. The second spectrogram of each group was obtained in an arc discharge. Here again the spark pair 1 $\mathfrak{S}$ – 2 $\mathfrak{P}$ is present, but with less intensity than the arc line 1 *S* – 2 *P*. The inner two spectrograms are the ordinary arc and spark spectra of magnesium. Certain lines which are extremely intense in these spectra are readily seen to be absent when the amount of the metal is decreased, as in the two outer spectrograms, so that the phenomenon is not at all a matter of relative intensity with the ordinarily brighter lines persisting when the dilution increases. Similar results may be noted with calcium. The spark pair 1 $\mathfrak{S}$ – 2 $\mathfrak{P}$ and the single line 1 *S* – 2 *P* are prominent. Another calcium pair is also present, belonging to a subordinate series in the spark spectrum. This is due to the fact that more calcium is present than is necessary to produce the raies ultimes alone. At percentages of Ca>0.001 per cent, this second pair is always found, while for lower percentages only the raies ultimes are present, one of the empirically determined and useful facts of spectroscopic analysis.

In addition to these lines we note the appearance of the first pair of the principal series of both copper and silver. By analogy one would conclude that the sensitive lines shown for the other impurities should also belong to fundamentally important series of a similar type, but unfortunately these are unknown.

Figure 27 shows some long and short lines in the spark spectra of two

different alloys. For example, the three aluminum lines λ 3587, 3602 and 3613 in the upper spectrogram appear at the electrodes only, while the lines λ 3944, 3962 are long lines extending throughout the space between the electrodes. The latter constitute the first pair of the 2d Subordinate series while the classification of the former is unknown. In the lower spectrogram one may readily note the difference in appearance of the lead lines λ 4019, 4168 and the lines λ 4245, 4387, the latter being "short" lines, as is evidenced by the very much higher intensity at the poles.

This figure is given simply to indicate the general appearance of long and short lines. Unfortunately photographs, suitable for reproduction, are not available to the authors to clearly illustrate the present discussion of the physical behavior of long lines. Most of the work in this field has been done either with elements for which the series relations are unknown or has embraced a too limited portion of the spectrum.

A careful study of Table XXV shows that some fundamentally important series lines do not appear to be raies ultimes, for example the line $1\ S - 2\ p_2$, λ 4571 of magnesium. Why this should be true is not apparent. In fact the true physical significance of all the foregoing phenomena is not evident, and will involve further study.

We probably have in the arc or spark a distribution of potential in which most of the gradient is confined to the anode and cathode, with very little drop in the arc itself. Consequently the electrons, except near the electrodes, may not accumulate velocities exceeding the resonance potentials of the impurities. Accordingly lines of the arc and spark spectra other than those of the so-called fundamental type can not be excited throughout the central portion of the arc. Furthermore, the excitation of these fundamentally important lines may give rise to resonance radiation which through absorption and re-emission becomes uniformly distributed throughout the volume of vapor, thus accentuating the presence of the "long lines."

We are able to offer only a suggestion in regard to the origin of the raies ultimes. Suppose Zn occurs as an impurity in Mg to the extent of 1 Zn atom for every 100,000 Mg atoms. The arc spectrum will show all arc lines of Mg and the Zn arc lines $1\ S - 2\ p_2$ and $1\ S - 2\ P$, the raies ultimes of Zn. We may assume that since the electrons emitted by the cathode can not be discriminatory, the probability of collision with a metal atom is proportional to its concentration.

Hence in general an arc line of Zn will be 1/100,000 as intense[35] as the

[35] Neglecting modifying factors such as differences in ionization potential, cross section of atom, etc.

corresponding line in Mg, and would certainly not be observed. But in the case of resonance lines (lines absorbed and re-emitted by the surrounding vapor) the above reasoning does not hold. The absorption factor increases with the concentration. Hence only for extremely rare vapors is the intensity of emission proportional to the concentration, and with increasing partial pressure of the absorbing atoms a stage is soon reached where the increase in intensity becomes relatively small. The problem of the arc discharge is so complicated that a mathematical treatment of the subject is out of the question, but in the much simpler case of flame spectra (Chapter VII) the emission of resonance lines under thermal excitation is treated in some detail. The theory is applied only to dilute vapors, but the equations used indicate the manner in which the absorption factor would enter with increased concentration. These considerations apply equally well to either electrical or thermal excitation.

The quantitative results for extremely dilute vapors in flames indicate that in an arc the thermal excitation alone would suffice to explain the appearance of the raies ultimes of minute traces of an element. This fact together with the above mentioned absorption factor gives at least a qualitative explanation for the appearance of resonance lines of an impurity, with an intensity comparable to that of the arc lines of a concentrated vapor. The fact that some of the raies ultimes listed in Table XXV are subordinate series lines is not necessarily in contradiction to the above theory. Resonance lines of normal atoms are indeed principal series lines, but if the resonance potential is very low, many of the atoms in an arc will be in the 2 p state. These excited atoms will absorb and re-emit subordinate series lines. For such atoms, lines of subordinate series will possess the characteristics of "raies ultimes" and "long lines."

Chapter VI

Cumulative Ionization

Cumulative ionization denotes the process whereby atoms may be ionized by successive stages of excitation. (1) A valence electron may be ejected to an outer orbit such as 2 p_2 by electronic collision and the excited atom thus formed may collide with a second electron having a velocity sufficient to completely eject the valence electron. This process is known as *ionization by successive impact.* (2) A valence electron may be ejected to an outer orbit by absorption of radiation, and the excited atom thus formed may collide with an electron having a velocity sufficient to complete the process of ionization. Compton designates this as *photo-impact ionization.* (3) The valence electron may be ejected to an outer orbit by absorption of radiation, and the process of line absorption continued until the atom is ionized. This may be called *ionization by successive photo-electric action.* These processes may be of course jointly involved with several absorptions of radiation followed by an electronic impact.

K. T. Compton[1] has made a mathematical analysis of the processes (1) and (2). He has derived an expression, in terms of measurable quantities, which gives the fractional number of gas atoms at any instant in the excited state, and hence in a condition for ionization by electronic impact below the ionization potential; (1) as a result of electronic collision and (2) as a result of absorption of resonance radiation from neighboring atoms which have been previously excited by electronic impact. Necessarily rather questionable assumptions must be made in order to simplify the analysis, but the results are probably somewhere near the correct order of magnitude, which is sufficient for the present. The following outlines Compton's method in the treatment of the problem.

Figure 28 represents a cylindrical, two-electrode discharge tube, filled with vapor, in which A is the anode and C the hot wire cathode, mounted concentrically. If the accelerating field V is *less* than the

[1] Phys. R., 20 (1922).

ionization potential V_i but *greater* than the resonance potential V_r, inelastic collisions will occur resulting in excitation of the atoms and subsequent emission of radiation. For a given applied potential difference V, an individual electron will attain a velocity V_r at a certain distance from the cathode. However, since an impact with an atom may not occur at precisely the instant the electron attains this velocity, and for another reason explained later, we shall have for all the emitted electrons a *region* of effective collision, a small volume inclosed by two concentric cylindrical surfaces, represented by the shaded portion of the diagram.

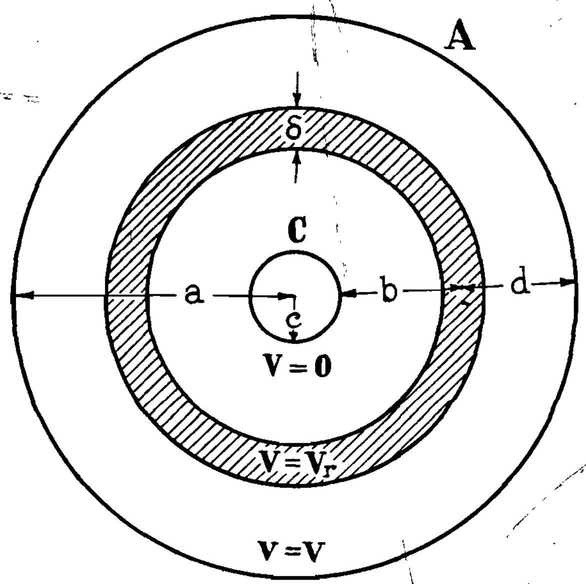


FIG. 28. Cross section of discharge tube.

EXCITATION BY ELECTRONIC IMPACT

Let the n electrons emitted per second by the cathode collide effectually in the shaded space of Figure 28. Excited atoms are accordingly produced which remain in the excited state for an average time interval τ second. If P denotes the fractional number of atoms which at any instant, for any reason whatever, are in the excited condition, then $n(1-P)$ atoms are excited per second by electronic impact, and the aggregate time of excitation of all the atoms is $n(1-P)\tau$. This divided by the total number of atoms in the shaded volume gives the fractional

number of atoms which at any instant are in the excited state as the direct result of electronic impact. Calling this fraction P_i, we have

$$P_i = \frac{n(1-P)\tau}{vNp} = \frac{n\tau}{vNp}, \qquad \text{approximately} \qquad (93)$$

where p is the gas pressure in mm Hg, N is the number of atoms per cm³ at a pressure of 1 mm Hg and v is the volume of the shaded cylindrical shell within which the effective impacts occur. If f is the length of this volume and δ its width, evidently

$$v = 2\,\pi(b + c)f\delta. \qquad (94)$$

From the distribution of potential in a concentric arrangement such as here considered we find

$$b + c = ae^{-\frac{V-V_r}{V}\ln\frac{a}{c}}, \qquad (95)$$

where a and c are the respective radii of the anode and cathode. The calculation of δ is more difficult, for it depends on the average distance which the electrons move beyond the point at which they have acquired the velocity V_r before making an effective impact, and also on the distribution of velocities of electrons which causes them to gain the critical velocity at different distances from the cathode. Compton derives the formula

$$\delta = \sqrt{\frac{\pi}{8}}\,\frac{l}{p} + \frac{\alpha T}{eV}(b + c)\ln\frac{a}{c}, \qquad (96)$$

in which

l = mean free path of an electron at a pressure of 1 mm Hg
αT = average kinetic energy of an atom at the cathode temperature T.

We accordingly obtain from Equations (93), (94) and (95)

$$P_i = \frac{n\tau}{2\,\pi(b + c)f\delta Np}, \qquad (97)$$

where δ may be computed from Equation (96). This gives the fractional number of atoms which at any instant are in the excited state as the direct result of impact.

Excitation by Absorption of Radiation

Impacts in the shaded layer produce radiation which is absorbed and re-emitted by atom after atom before escaping from the vapor so that, as a result of the activation of a single atom by direct impact, many other atoms are successively activated through absorption of the emitted radiation. Thus at any instant the fractional number P_r of *atoms in the excited state as a result of absorption of radiation should* be greater than P_i if much absorption occurs.

The quanta of radiation are passed on from atom to atom, diffusing through the vapor in all directions in a manner analogous to the diffusion of a foreign gas, and accordingly the same mathematical procedure may be employed in the treatment of the two problems. A beam of light passing through an absorbing or scattering medium decreases in intensity according to the law

$$I = I_0 e^{-kx}, \tag{98}$$

where k is the absorption coefficient. A stream of particles passing through a gas is reduced by collisions or scattering according to the law

$$n = n_0 e^{-x/l}, \tag{99}$$

where l is the mean free path.

We may define ρ as the reciprocal of the absorption coefficient k, *i.e.* as the distance in which the intensity of a beam of monochromatic *radiation through a vapor at 1 mm pressure decreases to $1/e$ of its initial* value. By analogy to Equation (99), this is the mean free path of a quantum in a gas at 1 mm pressure, and the mean free path at p mm pressure is accordingly ρ/p. Although in our particular problem some of the atoms are excited and hence are incapable of absorbing or scattering resonance radiation, the fractional number in this condition is too small to alter materially the value of the mean free path ρ/p strictly applicable to normal atoms. Accordingly the average speed $\bar{c}$ of the radiation is equal to the distance ρ/p divided by the time τ in which an atom on the average remains in the excited condition. We may therefore apply the diffusion equation:

$$\iint \frac{1}{3}\frac{\rho}{p}\bar{c}\frac{\partial N'}{\partial \eta}\, dS = -\iiint R\, dx\, dy\, dz, \tag{100}$$

where N' is the number of excited atoms per cm^3 at any point at any instant in the vapor of pressure p, R is the net rate at which atoms are excited by direct electron collision and η is the outward normal to the closed surface over which the surface integral and within which the volume integral are taken. For details as to the application of Equation (100) in the solution of our problem, the original paper must be consulted. Compton shows that with reasonable assumptions and for V not very much greater than V_r the following expression is derivable.

$$N' = \frac{3}{2}\frac{p^2 n\tau}{\pi f \rho^2}\frac{V - V_r}{V}\, ln\, \frac{a}{c}. \tag{101}$$

Since there are Np atoms, N' of which at any instant are in the excited state, we obtain

$$P_r = \frac{N'}{Np} = \frac{3}{2}\frac{pn\tau}{\pi f N \rho^2}\frac{V - V_r}{V}\, ln\, \frac{a}{c}. \tag{102}$$

Numerical Magnitudes

The relative importance of P_r and P_i is **obtained on dividing** Equation (102) by Equation (97) as follows.

$$\frac{P_r}{P_i} = \frac{3\,p^2(b+c)\delta}{\rho^2}\,\frac{V-V_r}{V}\,ln\,\frac{a}{c}\,. \qquad (103)$$

As mentioned on page 89 Wood found that the intensity of the resonance radiation of mercury λ 2537 was reduced to $\frac{1}{2}$ its value in traversing a distance of 0.5 cm through mercury vapor at a pressure 0.001 mm Hg. This datum in the above defined units makes $\rho = 0.0007$. Reasonable constants for the dimensions of the discharge tube are: $a = 0.5$ cm; $c = 0.025$ cm; $f = 1$ cm. For mercury $V_r = 4.9$ volts. Let the total applied potential exceed this by one volt, *i.e.* $V = 5.9$.

On carrying through the computations involved in Equation (96) it is found that δ is roughly constant, averaging about $\delta = .04$ for a wide range of pressure and temperature of the cathode. We thus obtain from (103)

$$\frac{P_r}{P_i} = 40{,}000\,p^2$$
$$= 40{,}000 \text{ at 1 mm pressure}$$
$$= 4{,}000{,}000 \text{ at 10 mm pressure.}$$

Now the probability of an electron colliding with an excited atom and of ionizing below the ionization potential is proportional to $P_r + P_i$. It is therefore evident that ionization by photo-impact is relatively of far greater importance than ionization by successive impact especially at the higher vapor pressures.

We shall now consider Equation (102) to determine whether ionization by photo-impact is, in itself, an important factor in arc phenomena. One serious difficulty here is our inadequate knowledge of the quantity τ an estimate of which was stated in Chapter IV to be 10^{-8} seconds. Using this value and the data given above we accordingly obtain from (102)

$$P_r = 5\cdot 10^{-3}\,\frac{pn}{N} = 10^{-19}\,pn.$$

The number of electrons n leaving the cathode in the absence of any ionization is limited by the space charge and may be computed from the Langmuir formula $n = 1.8\cdot 10^{14}\,V^{\frac{3}{2}} = 2.5\cdot 10^{15}$ in which the constants of the particular apparatus have been substituted. This relation is strictly true only in vacuo, and actually, the current will be somewhat

less since the presence of the gas around the cathode reduces the rate of escape of electrons. We finally obtain for P_r in this favorable case:

$$P_r = 2.5 \cdot 10^{-4}\, p,$$

or at a pressure of 2 mm Hg, $P_r = 5 \cdot 10^{-4}$. If $\tau = 6 \cdot 10^{-7}$ (cf. Stark[2] for work with helium) this value should be increased by a factor of 60.

Arcs below the Ionization Potential

It is a well-known observation that arcs in vapors may be struck when the applied potential is only slightly greater than the resonance potential. We shall show that the computed value of P_r is sufficient to explain this phenomenon. If P_r represents the fractional number of excited atoms at any instant and n the number of electrons emitted per second by the cathode in the absence of ionization, the number of electronic collisions per second in the shaded space of Figure 28, which occur with excited atoms, is $n\,P_r$. If $V > (V_i - V_r)$, these collisions result in the production of nP_r ions per second.

The ionization of an atom increases the current in two ways, first by releasing an electron and second by creating a slowly moving positive ion and thus neutralizing a part of the negative space charge which limits the thermionic emission. The positive ion remains in the field $4\sqrt{3680\,M}$ times as long as an electron, where M is the atomic weight of the atom-ion. One ion accordingly neutralizes the effect on the space charge of $4\sqrt{3680\,M}$ electrons. This permits the emission of more electrons from the cathode, some of which in turn collide with excited atoms, produce more ions and release more electrons. Compton shows that under these conditions the total number n' of electrons leaving the cathode per second is

$$n' = \frac{n}{1 - 4\sqrt{3680\,M}\,P_r}, \qquad (104)$$

where P_r as before is the fractional number of atoms which at any instant are excited by the radiation produced by an emission of n electrons per second, that is, in the absence of any cumulative ionization. As P_r is increased, the ratio n'/n increases more and more rapidly, becoming infinite at $P_r = 1/4\sqrt{3680\,M}$ were the emission not limited physically by the value corresponding to the saturation thermionic current at the temperature of the cathode. With mercury such a condition is reached when $P_r = 2.91 \cdot 10^{-4}$, whereas our computed value

[2] Ann. Physik, 49, p. 731 (1916).

of P_r at 2 mm pressure was nearly double this. The value $P_r = 5 \cdot 10^{-4}$ was computed, however, with very favorable assumptions. If P_r is only $2.9 \cdot 10^{-4}$ we find by Equation (104) that $n'/n = 1000$. Observed values range roughly from 2 to 100. The observed rapid increase in current just before the arc strikes is accordingly amply explained by cumulative ionization of the photo-impact type.

This rapid increase in ionization and resulting production of ions thus neutralizes the space charge, and as the electron emission is limited by its saturation value, finally develops a positive space charge. When the space charge becomes positive, the potential drop is concentrated at the cathode so that the electrons attain their critical speed within a short distance from the cathode. This concentration of the region of effective impacts tends further to increase the probability of cumulative ionization. At the same time the temperature of the cathode is raised by the bombardment of the positive ions[3] which again increases n and P_r. We now have a condition of instability: the arc strikes, and the complete arc spectrum of the vapor may be produced below the ionization potential, at a potential $V = V_i - V_r$.

On account of the concentration of the potential gradient near the cathode as soon as a large number of ions are formed, electrons more nearly attain the full velocity of the impressed field before the first collisions with atoms occur. Somewhat the same distribution of potential is produced as that obtained in a more controllable manner by the use of an auxiliary electrode, as shown in Figure 22. Hence as the applied voltage is increased to V* corresponding to 1 $\mathfrak{S}$ for the alkali earths, enhanced lines may appear. The favorable condition for excitation of enhanced lines in a two electrode arc is high current density. The high current involves a large number of ions which neutralize the negative space charge and increase the potential gradient at the cathode. This well-known method for exciting enhanced lines has led to some misapprehension as to their origin. Many investigators have considered the purely incidental effect of high current to be the prime factor in the *physical* process of the excitation.

Ionization by Successive Photo-electric Action

The mathematical analysis of this process is so involved that the results are not readily interpreted. However, there is no doubt from the experimental standpoint that the phenomenon is of importance. We may have several absorptions of radiation followed by an electronic

[3] The beginner usually burns up the cathode and an ammeter at this stage.

impact which completes the ionization process, or without any electronic impact whatever most of the arc lines may be produced, under proper experimental conditions, showing that the valence electron may be driven to a remote outer orbit if not completely ejected.

A notable example of the latter process is the experiment of Fuchtbauer[4] who observed the emission of the mercury arc lines as a result solely of the absorption of radiation. This was considered in detail in Chapter IV, the last half of which is intimately concerned with the experimental verifications of this theory of successive photo-electric action. In the case of sodium, for example, the atom absorbs a quantum of D-radiation resulting in the ejection of a valence electron to the $2\ p$ orbit. Before the time interval τ elapses, a second quantum may be absorbed. This may have a frequency corresponding to any term in any series converging at $2\ p$. For example it *may be* the first term of the first subordinate series $2\ p - 3\ d$, in which case the valence electron is ejected to the $3\ d$ orbit, et cetera. At any stage in this process of absorption, in an arc, an electronic impact may occur, assisting in the process of the ejection of the valence electron.

Further Conclusions

We have noted above that an arc may be struck below the ionization potential if the applied voltage $V > (V_i - V_r)$. With mercury $V_i - V_r = 10.3 - 4.9 = 5.4$ volts. The phenomenon of absorption, however, under suitable experimental conditions, reduces this minimum voltage to V_r or 4.9 volts. The 4.9 volt impacts, indirectly through the absorption of the resulting radiation, maintain a large number of atoms with the valence electron in the $2\ p_2$ orbit. A 4.9 volt impact with such an excited atom is capable of ejecting an electron to the $3\ s$ or $4\ d$ orbits. The radiation subsequently resulting from this ejection will maintain a proportion of excited atoms with electrons in these higher energy levels. A collision of 4.9 volts with such atoms is more than sufficient to ionize. Accordingly arcs *may be* struck at the lowest resonance potential of the vapor.

A final observation is the well-known fact that arcs once struck will continue to operate even when the *applied* voltage is less than the resonance potential. The most important factor here, in addition to the points brought out in the foregoing discussion, is the photo-electric effect of the resonance radiation on the cathode. Van der Bijl[5] mentions that

[4] Physik. Z., 21, pp. 635–8 (1920).
[5] Phys. R., 10, p. 546 (1917).

λ 2537 of mercury should liberate photo-electrons from a calcium-coated cathode with an initial velocity of 1.5 volts, so that an arc in mercury once started, might be maintained at 4.9 − 1.5 = 3.4 volts. Radiation of wave-length as short as λ 1188 is present in the arc so that some photo-electrons of still higher velocity are liberated. Still further, a few high velocity electrons are emitted in accordance with the Maxwellian distribution of velocities, as shown by Equation (86). And finally the ions created in falling into the cathode, may liberate electrons of considerable speed. All of these factors must be considered in interpreting the action of certain rectifiers which may be operated at astonishingly low voltages. In this case we have in addition the favorable fact that the maximum voltage is greater than the measured root mean square voltage. However, a discussion of rectifiers is beyond the scope of this book.

The conclusion to be drawn from the foregoing considerations is that the phenomenon of absorption of radiation plays an important rôle in arc characteristics and emission of radiation. Cumulative ionization of the photo-impact type becomes a controlling factor with high electronic emission and vapor pressure. It is possible that ionization by successive impact is of some importance at very low pressure, but in general, compared to the effect of absorption of radiation, its action is insignificant.

This latter statement of course applies only to simple ionization. Successive or multiple ionization is readily produced by successive impact as shown in the appearance of the enhanced spectrum of magnesium at 14.97 volts (cf. discussion of Figure 23). The probability of multiple ionization by successive impact depends upon the time of recombination for the ion formed at the first impact. This time interval, which corresponds to τ, may be relatively very large, depending upon the probability of a collision between an ion and an electron of *small* kinetic energy. It should be accordingly a function of the design of any particular apparatus. Child[6] has made extensive experiments with a mercury arc excited by a sixty cycle current. By examining the intensity of the arc lines at various phases of the cycle he found that the minimum intensity lagged behind the time of zero current and voltage by an interval of 1/1800 second. Experiments of other observers also indicate that we are here dealing with a time interval of an entirely different order of magnitude than 10^{-8} seconds, the value of τ for a neutral atom.

[6] Phys. R., 9, pp. 1–14 (1917).

Chapter VII

Thermal Excitation

Thermodynamic Considerations

The absolute entropy of a mol of perfect gas is given by the following formula:

$$S = \tfrac{5}{2} R \ln T - R \ln p + \tfrac{3}{2} R \ln M + S_1, \qquad (105)$$

where M is the molecular weight, $R = 1.985$ *cal. deg*$^{-1}$, p throughout this chapter except where otherwise noted, the pressure expressed in atmospheres, T the absolute temperature, and $S_1 = -3.2$ *cal. deg*$^{-1}$. Evidence for the value of S_1 and its constancy with various monatomic gases has been discussed by Tolman[1] and others.

It has been recognized for some time in mathematical treatments of thermionic emission, thermoelectricity, contact potential, etc., that electrons may be considered as a gas, the laws of which they obey in detail, one example being the Maxwellian distribution of velocities. The pressure of this gas in any laboratory experiment is exceedingly small, of the maximum order of magnitude 10^{-8} atmospheres, so that considering an electronic atmosphere as a perfect gas should be open to no objection.

From data on the thermionic emission of tungsten, tantalum and molybdenum, and measurements of the cooling of the filament, due to the latent heat of vaporization of the electrons, Tolman[2] shows that the entropy of electron gas is given by Equation (105) where S_1 has the same value as for a perfect monatomic gas. The value of M for electrons is of course expressed on the scale $M = 1.008$ for the hydrogen atom, whence $M_e = 5.46 \cdot 10^{-4}$.

[1] J. Am. Chem. Soc., 42, pp. 1185–93 (1920).
[2] J. Am. Chem. Soc., 43, pp. 1592–1601 (1921).

Accordingly if it is possible to determine the absolute entropy of both gases and electrons by Equation (105), we may predict from thermodynamic considerations the extent to which a reaction such as ionization may proceed at any desired temperature. Tolman's[3] derivation of the reaction-isochore is given in the following paragraphs.

Consider a reversible reaction of the type

$$Ca = Ca^{+} + E^{-} - J, \qquad (106)$$

where Ca, Ca^{+} and E^{-} are respectively gram mols of neutral calcium atoms, simply charged positive calcium ions, and electrons, and J is the work, expressed in calories, required to ionize one mol of calcium atoms. If f is the value of the faraday, V_i the ionization potential in volts, and $j = 4.183$, the mechanical equivalent for converting joules to calories, we have

$$J = \frac{fV_i}{j} = \frac{96500\ V_i}{4.183} = 23070\ V_i. \qquad (107)$$

This is simply a more direct method of deriving Equation (69).

The heat ΔH of the reaction at constant pressure and at temperature T is:

$$\Delta H = J + \tfrac{5}{2} RT. \qquad (108)$$

The quantity J is accordingly the increase in heat content of the system at the absolute zero and $\frac{5}{2} RT$ the value of $\Delta c_p T$ where c_p is the specific heat of a perfect gas at constant pressure.

The change in entropy of the system when the reaction occurs at constant temperature, obtained directly from Equation (105), is:

$$\Delta S = \tfrac{5}{2} R ln T + \tfrac{3}{2} R ln M_e + S_1, \qquad (109)$$

in which we have neglected the slight difference between the molecular weights of the ionized and the neutral atom.

We have the following fundamental, definitory equation of thermodynamics[4] connecting free energy with heat content and entropy:

$$\Delta F = \Delta H - T\Delta S. \qquad (110)$$

Introducing the values of ΔH and ΔS from Equations (108) and (109) we obtain

$$\Delta F = J - \tfrac{5}{2} RT ln T + (\tfrac{5}{2} R - \tfrac{3}{2} R ln M_e - S_1)\, T. \qquad (111)$$

[3] J. Am. Chem. Soc., 43, pp. 1630–2 (1921).
[4] This is a generally accepted definition among physical chemists.

The equilibrium constant K_p by definition takes the **following** form for a reaction of the type given by Equation (106)

$$K_p = \frac{p^+ \cdot p^-}{p}, \tag{112}$$

where p^+, p^-, and p denote respectively the partial pressures in the equilibrium state of the ions, the electrons and the neutral atoms.

Now for any reaction there is a perfectly definite relation expressed by Equation (113), between the change in free energy and the equilibrium constant. The derivation of this relation, which is familiar to chemists, consists simply in the manipulation of thermodynamic equations, and can be found in text books on physical chemistry.

$$\Delta F = -RTlnK_p. \tag{113}$$

Substituting the value of ΔF from Equation (111) we obtain:

$$lnK_p = -\frac{J}{RT} + \frac{5}{2}lnT - \left(\frac{5}{2} - \frac{3}{2}lnM_e - \frac{S_1}{R}\right). \tag{114}$$

On changing to common logarithms, expressing J in terms of V_i, and substituting the other numerical magnitudes mentioned above, we find,

$$log\ K_p = log\frac{p^+ \cdot p^-}{p} = -\frac{5050\ V_i}{T} + 2.5\ log\ T - 6.69. \tag{115}$$

This is the reaction-isochore by which we may compute the degree of ionization of any monatomic vapor as a function of the temperature. If x represents the fractional number of the atoms which are ionized, we may write

$$log\frac{x^2}{1 - x^2}P = -\frac{5050\ V_i}{T} + 2.5\ log\ T - 6.69, \tag{116}$$

where P is the total pressure, *i.e.* $P = p^+ + p^- + p$.

Simple Ionization

Saha[5] has employed this equation to compute the degree of ionization of various elements at high temperatures. As a particular example we give in Table XXVI his computations for calcium for which the ionization potential is 6.1 volts. The degree of ionization is expressed in percentage, pressure in atmospheres, and temperature in degrees absolute.

[5] Proc. Roy. Soc., 99, pp. 135–53 (1921).

TABLE XXVI

Thermal Ionization of Calcium Expressed in Percentage

Pressure / Temperature	10	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-6}	10^{-8}
2000°					$5\cdot10^{-4}$	$1.4\cdot10^{-3}$		
2500					$2\cdot10^{-2}$	$7\cdot10^{-2}$		
3000					$3\cdot10^{-1}$	1	9	
4000				2.8	9	26	93	
5000		2	6	20	55	90		
6000	2	8	26	64	93	99		
7000	7	23	68	91	99			
7500	11	34	75	96				
8000	16	46	84	98				
9000	29	70	95					
10000	46	85	98					
11000	63	93						
12000	76	96			Complete Ionization			
13000	84	98						
14000	90							

As is evident from Equation (116), the percentage ionization increases with (1) increasing temperature, (2) decreasing pressure, and (3) decreasing ionization potential. Calcium has a medium low ionization potential. It is therefore interesting to contrast the figures of Table XXVI with those of Table XXVII for atomic hydrogen which has an ionization potential of 13.5 volts. At the temperatures given, the dissociation $H_2 \rightarrow 2\ H$ can be readily shown to be complete, so that we do not need to consider the molecule.

TABLE XXVII

THERMAL IONIZATION OF HYDROGEN EXPRESSED IN PERCENTAGE

Pressure / Temperature	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}
7000				1	4	12
8000			2	5	18	50
9000		2	6	20	63	90
10000	2	6	17	49	87	99
12000	9	28	68	94		
14000	27	65	93			
16000	55	90				
18000	80	97				
20000	92	Complete Ionization				
22000	97					

It is thus seen that very much greater temperatures are required to produce the same degree of thermal ionization in hydrogen than in calcium vapor on account of the higher ionization potential of the former. Caesium, which has the lowest ionization potential of all the elements so far measured, should be completely ionized at about 4000° and 10^{-4} atmospheres, while about 20,000° at the same pressure should be necessary for helium, which has the highest known ionization potential.

DOUBLE IONIZATION

The analysis for the simple ionization of atoms by thermal excitation may be extended so that the fractional number of atoms which are doubly ionized may be computed. Using calcium as an example, we have the reactions:

$$\left.\begin{aligned} Ca &= Ca^{+} + E^{-} - V_i f/j \\ Ca^{+} &= Ca^{++} + E^{-} - V_i^* f/j \end{aligned}\right\}. \tag{117}$$

Here V_i^* corresponds to the work required to remove the second electron from the atom after the first has been ejected. As discussed in the latter part of Chapter V, this is determined by the wave number 1 $\mathfrak{S}$ for metals of Group II (cf. Table XX). Its value is 54.2 volts for helium. The spectroscopic relations are unknown for metals of Group I, but probably the voltages should correspond to x-ray limits rather than to highest convergence frequencies of the enhanced spectra, as shown in column 7 of Table XXII. Nothing is known of the values of V_i^* for other elements.

If x and y represent the fractional number of *Ca* atoms which are, respectively, simply and doubly ionized, it may be shown that

$$log \frac{x\,(x + 2\,y)\,P}{(1 - x - y)\,(1 + x + 2\,y)} = - \frac{5050\,V_i}{T} + 2.5\,log\,T - 6.69, \quad (118)$$

$$log \frac{y\,(x + 2\,y)\,P}{x\,(1 + x + 2\,y)} = - \frac{5050\,V_i^*}{T} + 2.5\,log\,T - 6.69. \quad (119)$$

If we confine our attention to the temperature and pressure ranges where the proportion of neutral *Ca* atoms is very small, we may put, approximately, $x + y = 1$. Equation (119), which then alone need be considered, takes the form:

$$log \frac{y\,(1 + y)\,P}{(1 - y)\,(2 + y)} = - \frac{5050\,V_i^*}{T} + 2.5\,log\,T - 6.69. \quad (120)$$

Since V_i^* is always considerably greater than V_i it will necessarily require a much higher temperature to produce the same degree of double ionization as of simple ionization. For example with helium at 10^{-4} atmospheres but 77% of the atoms will be doubly ionized at 30,000° while simple ionization is practically complete at 20,000°. Table XXVIII gives the temperatures at which several elements will be simply and doubly ionized to the extent of 50%. By means of the above equations one will readily find that if 50% of the atoms are just simply ionized, practically none will be doubly ionized (0.1% and less) and the remaining 50% will be normal. Similarly if 50% are doubly ionized, the other 50% will be simply ionized with practically no neutral atoms present. The temperatures here given are comparatively high. If lower pressures had been selected, the temperatures would have been very much lower, as indicated in the table by the large temperature change from a pressure of 1 to 0.01 atmosphere.

TABLE XXVIII

SIMPLE AND DOUBLE THERMAL IONIZATION

Element	50% simply ionized Practically 50% normal		50% doubly ionized Practically 50% simply ionized		98% doubly ionized	
	$P = 1$	$P = 0.01$	$P = 1$	$P = 0.01$	$P = 1$	$P = 0.01$
Li......	7800° abs	5300° abs				
Na......	7500	5100				
K......	6600	4400				
Cu......	10300	7100				
Rb......	6300	4300				
Ag......	10100	7000				
Cs......	6000	4100				
Au......	11000	7800				
H......	16000	11500				
Mg......	10200	7100	18000	13000	26500	17000
Ca......	8600	5900	15000	10700	22000	14000
Zn......	12000	8400	21000	15300	30500	20000
Sr......	8100	5500	14000	10000	21000	13500
Cd......	11600	8100	20000	14700	29500	19000
Ba......	7500	5200	13000	9200	20500	12500
Hg......	13000	9200	23000	16500	33000	22000

THERMAL EXCITATION WITHOUT IONIZATION

The fact that we have been able to derive from thermodynamic considerations certain quantitative data in regard to thermal ionization, which, as will be apparent later, seem to interpret satisfactorily phenomena heretofore very puzzling, does not of course argue that heat in itself drives an electron out of the vapor atom. All that the thermodynamic treatment has done is simply to give a statistical survey of the actual state at any temperature without the introduction of any postulates as to *how* the ionization is produced physically. Since at any high temperature free electrons are admittedly present in the vapor, it is likely that the ionization is accomplished in part by collision with these electrons, the speed of which, and hence the number capable of ionizing, increases rapidly with the temperature. Also cumulative ionization involving absorption of radiation must play an important rôle at high pressure, as discussed in Chapter VI. Howbeit, it is of interest to con-

sider in the above statistical manner this indirect effect of temperature on the excitation of atoms without ionization. For example, let Na' represent a sodium atom in which the valence electron is in the 2 p instead of the normal 1 s orbit. For a mol of the vapor we have the reversible reaction:

$$Na = Na' - J_r, \tag{121}$$

where $J_r = fV_r/j$, the quantity V_r being the resonance potential expressed in volts. Since both the normal and the excited atoms are assumed to act as perfect gases, there is no change in volume or pressure and no external work is done. Accordingly[6] instead of Equations (108) and (109) we have:

$$\Delta H = J_r, \tag{122}$$

$$\Delta S = 0. \tag{123}$$

Substituting these values in Equation (110) we obtain:

$$\Delta F = J_r \tag{124}$$

and from (113) it follows that

$$J_r = -RT\, ln\, K_p = -RT\, ln \frac{p'}{p}, \tag{125}$$

where p' and p denote respectively the partial pressures of the excited and normal atoms. If we confine our attention to such a temperature range that p' is small compared to p we may consider p to be approximately the total pressure and p'/p the fractional number of excited atoms, whence,

$$\frac{p'}{p} = e^{-J_r/RT}, \tag{126}$$

or

$$N' = Ne^{-J_r/RT}, \tag{127}$$

where N is the total number of atoms, of which N' are excited, the latter having an increase in energy of J_r calories per mol of *excited atoms*.[7]

As an example we shall apply Equation (126) to sodium. Since V_r = 2.1 volts we find

$$\frac{p'}{p} = e^{-\frac{24400}{T}} \text{ for sodium.}$$

Table XXIX gives the fractional number of atoms, computed from this formula, which have an electron in the 2 p orbit.

[6] This method of derivation was suggested by Tolman.

[7] An expression equivalent to this results directly from probability considerations. See any treatise on quantum theory, for example, Tolman, Optical Soc. Am. and R. S. I., May (1922).

TABLE XXIX

THERMAL EXCITATION OF SODIUM

Temperature	Fractional number of atoms with electron in 2 p orbit
800 abs	$5 \cdot 10^{-14}$
1000	$2 \cdot 10^{-11}$
1500	$1 \cdot 10^{-7}$
2000	$5 \cdot 10^{-6}$
3000	$3 \cdot 10^{-4}$

A similar table might be computed for an orbit of greater energy level illustrated by Figure 5, for example for 2 s , or 3 d, in which case we should find a higher temperature necessary to maintain the same concentration of excited atoms.

FLAME SPECTRA

If a metal is vaporized in a bunsen flame, an emission spectrum is produced. Usually this consists of the first pair 1 s − 2 p of the principal series for the alkalis and 1 S − 2 p_2 and sometimes 1 S − 2 P for the metals of Group II. Observations on the alkalis are a matter of common experience. The slightest trace of sodium vapor in the bunsen gives rise to the D-lines. Using a very simple device of McLennan and Thomson[8] in which a small furnace surrounding the bunsen maintains the heat necessary to vaporize the metal at a slow and constant rate, the flame spectra of the elements of Group II are readily observed, as indicated by F in the last column of Table XVI.

In general we may conclude that the fundamentally important lines, from the standpoint of atomic theory, are those which appear in the low temperature flame. These same lines determine the values of the resonance potentials, as discussed in Chapter III. They appear in the arc below ionization, as shown in Figures 23 and 24. They are prominent absorption lines of the normal vapor and are readily reversed, as shown in Figures 14 and 15. They are the "long" lines and the "raies ultimes" as discussed in the latter part of Chapter V. They are the result of the ejection of an electron to an orbit of next higher energy level than the normal state of the unexcited atom.

[8] Proc. Roy. Soc., 92, pp. 584–90 (1916).

These lines by no means appear in the flame because they normally are the most intense lines of the arc spectrum and hence by contrast only *seem* to be excited alone. In fact usually they are *not* the bright lines of the arc; especially is this true of the metals of Group II. Furthermore one may photograph a *low* temperature sodium flame until the plate is "burned up" at the D-line and only a slight trace of other lines can be detected. We may conclude that in general the ratio of intensities of these fundamental lines to other lines is extraordinarily high in the flame. We have in the bunsen another method of producing single-line or two-line spectra.

When a salt is injected in the flame we obtain again the simple single-line spectrum of the metal, as shown in Figure 28 A, prepared by Meggers. Under certain conditions, however, other lines appear faintly, for example lines of the subordinate series. This is readily explained by the fact that dissociation of the salt, such as $NaCl$, by the flame, gives rise to Na^+ and Cl^-. If the sodium ion captures an electron, it is thereby able to emit any line of the arc spectrum. Zahn[9] estimates that each sodium atom in a bunsen flame fed with $NaCl$ emits on the average 2000 quanta of D-radiation per second. It is readily believable with the minute partial pressures of sodium or chlorine in a flame (order of magnitude 10^{-6} mm Hg and less) that the probability of a sodium atom capturing a chlorine atom and forming $NaCl$ to be again dissociated is comparatively small. In other words the number of times a reaction of the form

$$NaCl \rightarrow Na^+ + Cl^-,$$

occurs, which may involve a subsequent reaction

$$Na^+ + E^- = Na,$$

and the emission of all arc lines is small compared to the number of times the reversible reaction

$$Na' \rightarrow Na$$

takes place with the emission of the D-lines. Hence while the dissociation of $NaCl$ does give rise to all arc lines, the formation of Na', having the short life $\tau = 10^{-8}$ seconds (page 93) is so much more frequent that the intensity of these fundamental lines is extraordinarily high relative to the other arc lines. The main service of the salt is accordingly in furnishing a carrier for the metal and the *immediate* spectroscopic consequence of the dissociation is incidental.

[9] Verh. Physik. Ges., 15, pp. 1203–14 (1913).

Again emphasizing that temperature in itself may not be the cause of the excitation of a neutral atom but rather is the source of some other direct cause, such as high electronic velocities, let us apply the foregoing statistical reasoning to the emission of light from a bunsen.

Zahn observed that when $6.9 \cdot 10^{13}$ sodium atoms per sec. were fed into a bunsen having a flame propagation of 510 cm/sec., a rate of emission of D-radiation resulted, amounting to 10^2 ergs/sec. cm^2, as shown by photometric measurements. He states that the bright flame was 3 cm long but does not give its radius. We shall assume the flame to be a cylinder 1 cm in diameter. Using the above figure for the rate of emission, we accordingly find that the total emission of the flame is 10^{14} quanta/sec., which is Zahn's experimental value expressed in other units.

The volume of the flame is 2 cm^3. Hence

$$\text{number of } Na\ atoms/cm^3 = \frac{6.9 \cdot 10^{13}}{2 \cdot 510} = 7 \cdot 10^{10} \text{ at any instant.}$$

Let us consider the temperature[10] of the flame as 2000° abs. Referring to Table XXIX we find that the fractional number of atoms in the 2 *p state at 2000°* is $5 \cdot 10^{-6}$.

Whence

$$No.\ excited\ atoms/cm^3 = 5 \cdot 10^{-6} \cdot 7 \cdot 10^{10} = 3.5 \cdot 10^5$$

and

$$total\ no.\ excited\ atoms\ (2\ cm^3) = 7 \cdot 10^5\ at\ any\ instant.$$

The average duration of life of an excited atom, as discussed in Chapters IV and VI, is $\tau = 10^{-8}$ seconds. Accordingly the number of excited atoms formed per second is $7 \cdot 10^5 \div 10^{-8} = 7 \cdot 10^{13} = 10^{14}$. This is equivalent to the number which pass into the normal state each second so that a total of 10^{14} quanta per second of D-radiation are produced within the flame. Let us see how many of these escape.

At atmospheric pressure the number of atoms per cm^3 is $2.7 \cdot 10^{19}$. Accordingly the partial pressure ($p\ mm$) of the sodium atoms is

$$p = \frac{7 \cdot 10^{10} \cdot 760}{2.7 \cdot 10^{19}} = 2 \cdot 10^{-6}\ mm\ Hg.$$

Let us assume that at any instant the quanta of radiation are uniformly distributed throughout the cylindrical volume. The quanta which escape will be those which pass through this volume to the outside boundaries without colliding with an atom. We shall assume that all

[10] We recognize the academic question here involved, but these computations are sufficiently inexact to permit the assignment of "temperature" to a state not in statistical equilibrium.

directions of propagation of the quanta are equally probable. Proceeding in a manner somewhat similar to that discussed in Chapter VI, Dr. K. T. Compton very kindly derived the following expression for the authors, giving approximately the fractional number of the quanta which escape.

Fraction =

$$\frac{1}{6}\left\{\frac{2\lambda}{h}\left(1-e^{-h/\lambda}\right)+\frac{2\lambda^2}{a^2}\left[\left(1+\frac{a}{\lambda}\right)\left(1-e^{-2a/\lambda}\right)-\frac{2a}{\lambda}e^{-a/\lambda}\right]\right\}.$$

In this formula λ is the mean free path of a quantum at the pressure p, as defined in Chapter VI, a is the radius of the cylindrical flame, and h its height.

In the discussion following Equation (99) we show that the mean free path of a quantum is ρ/p where ρ is an absorption constant and p is the pressure in mm Hg. Using Wood's value of ρ determined for mercury, we obtain for the mean free path $\lambda = (0.0007/p)$ cm. The value of ρ is probably of the same order of magnitude for the sodium and mercury resonance lines. Hence with the present data we have $\lambda = 7\cdot 10^{-4} \div 2\cdot 10^{-6} = 300$ cm for the mean free path of the quantum of D-radiation in this particular bunsen flame. The values of h and a are 3 cm and 0.5 cm respectively. Since λ is large compared to h or a, the above formula reduces to

$$\text{Fractional number escaping} = 1 - \frac{a}{\lambda} - \frac{h}{6\lambda}\,.$$

On substituting the values for these constants we find that 299/300 of the quanta produced in the flame are actually emitted. In contradistinction to arc phenomena discussed in the chapter on cumulative ionization, absorption is of very slight importance in flame spectra on account of the *low partial pressure* of the metal vapor. Accordingly we conclude that the bunsen flame of the type described should emit 10^{14} quanta/sec. The observed value was also 10^{14} quanta/sec. in complete agreement with theory.

Zahn has also made observations on the lithium flame. His data show that under specified conditions the total emission of the flame amounted to 10^{15} quanta/sec. for the red lithium line. The value computed theoretically in the manner illustrated above is 10^{16} quanta/sec., in satisfactory agreeement considering the assumptions involved.

If the temperature of a flame is increased by the addition of oxygen, other lines are readily excited. Many lines of the principal and subordinate series of sodium if not the complete arc spectrum, appear in the

oxy-acetylene burner fed with sodium or its salts, and the same phenomenon occurs with other elements. As the temperature is increased, the valence electrons are driven to successively higher energy levels, ultimately giving rise to the state of ionization. We may therefore correlate spectral lines with temperature, whether or not this be the direct cause for their production.

Spectral Lines Correlated with Temperature

If a metal vapor is gradually heated in a furnace we observe first the emission of a fundamental line of the type $1\ s - 2\ p$ or $1\ S - 2\ p_2$. This is also true when the vapor of a metallic salt is heated. We have found that the D-lines produced when NaCl is raised to 1000° C in vacuo are quite brilliant. Higher stages of temperature excitation progress through furnace spectra, which have been investigated by King[11] from 2000° to 3000° abs, spectra in the carbon arc at 3900°, chromospheric spectra at possibly 6000°, photospheric spectra at possibly 7000°, spark spectra, to stellar spectra at temperatures ranging up to 30,000°. Of course the correlation of arc and spark spectra with temperature is complicated by the superposed electrical excitation. As discussed in Chapter V, spark lines may be excited at very low temperatures, with a proper arrangement for producing high electronic velocities by electrical means. Hence our present classification must be considered as very qualitative.

Accordingly as the temperature of calcium vapor, for example, is increased, we should first have no emission, but rather absorption of fundamental lines belonging to the series $1\ S - mp_2$ and $1\ S - mP$. On further increase in temperature the line $1\ S - 2\ p_2$, λ 6573, should appear in emission and when the temperature is sufficient to maintain a fair proportion of electrons in the $2\ p_2$ orbit, lines of the subordinate series should show absorption. Gradually the line $1\ S - 2\ P$, λ 4227, puts in its appearance as an emission line, and finally all arc lines are excited when the thermal ionization becomes pronounced. If the temperature is further increased until a fair proportion of the atoms are simply ionized, the arc absorption and emission spectra fade, and fundamental lines of the enhanced spectra such as $1\ \mathfrak{S} - 2\ \mathfrak{P}_{1,2}$, λ 3968 and λ 3933 appear both in absorption and emission. Later other enhanced lines are excited, and if the process of heating is continued all the atoms will be doubly ionized. When this state is reached, steps

[11] Long series of papers in Astrophys. J. and Mt. Wilson Contrib.

begin toward triple ionization; the arc lines vanish and the ordinary enhanced lines should eventually fade, giving place to enhanced spectra of the "second type." There is no sharp division line between the various spectra. At any one temperature we may have spark lines from ionized atoms and arc lines from neutral atoms. If, however, the temperature is great enough to produce much double ionization it may be readily shown as pointed out earlier, that most of the atoms should be either simply or doubly ionized, with practically none in the neutral state. Hence if we have present the enhanced spectrum of the second type, all arc lines are absent. In other words but two types of spectra may be present simultaneously. Unfortunately as yet we have no knowledge of the higher types of enhanced lines, so that this deduction from theory cannot be verified.

If we select a fundamental arc line such as $1\ S - 2\ P$ and a fundamental spark line such as $1\ \mathfrak{S} - 2\ \mathfrak{P}$ and observe the ratio of intensity of the latter to the former, we should expect this ratio to increase with the temperature. This is verified qualitatively by King's results with furnace spectra and other data from the spectroscopic tables, as shown in Table XXX.

TABLE XXX

RATIO OF INTENSITY OF $1\ \mathfrak{S} - 2\ \mathfrak{P}$ TO $1\ S - 2\ P$

Element	Flame	Furnace ° Abs.			Arc 3900	Chromo-sphere 6000	Photo-sphere 7000
		2000	2300	2600			
Ca........	0	.06	.05	.06	.8	4	40
Sr.........	0	.03	.05	.06	.7	20	7
Ba........	0	.1	.1	.09	.8	20	4

SOLAR SPECTRA

As illustrated by Table XXVI the degree of ionization of an element depends greatly upon the pressure as well as the temperature. Thus the pressure differences existing in the sun may produce a wide variation in the type of spectrum excited. Also the quantity of the element present is of importance. Other things being equal we should expect lines from elements present in relatively large amounts to be the more prominent. If the element does not exist in the sun its spectrum will

be absent. However, the failure to detect arc lines of caesium for example is insufficient proof that the element is not present even in considerable quantity.

In the following we shall review some of the recent developments only in the roughest qualitative manner. For more detailed information, all necessarily qualitative however, the papers of Saha,[12] Russell,[13] Milne[14] and others should be consulted.

The solar spectrum should be characterized by lines of elements in a state corresponding to that at about 6000 to 7000°, and 4000° for a sun-spot. A considerable portion of the alkalis should be simply ionized, especially at the higher levels, where the pressure is less. Although much ionization is present, enhanced lines should not appear, for as discussed in Chapter V, the alkalis, with their single valence electron removed, are *not* in a condition to emit or absorb enhanced lines. This requires a further expenditure of energy of such magnitude that at least for sodium, potassium and lithium, for which the values are known, temperatures of 7000° are insufficient. One may fairly definitely state that enhanced lines of Na and K are absent in the sun. The arc spectra of Li, Na, K and a trace of Rb are present, arising in the small percentage of un-ionized atoms at solar temperatures. The failure to detect Cs may be due to the fact that the element is absent or that it may be nearly completely ionized and incapable of showing arc lines. The arc lines of the alkalis are strengthened in the sun-spots on account of the lower temperature and resulting lesser degree of ionization.

Table XXVI shows at 6000° a considerable proportion of ionized calcium vapor and the same is true for magnesium, barium and strontium. We find in the solar spectrum both arc and spark lines of these elements although for barium many of the arc lines are absent or very faint. The arc lines of Ca and Sr are strengthened in the sun-spots. As zinc has a high ionization potential, spark lines are probably absent, and the arc lines are weaker in the sun-spots.

The ionization potential of helium is so high that practically no atoms are ionized. Hence we may now understand the experimental fact that all enhanced lines of helium are absent.

Hydrogen also is not ionized except possibly at the very highest levels of the chromosphere, and then scarcely appreciably. We should expect to find all the lines of the Lyman series were it not for the absorption of the earth's atmosphere. A small proportion of the atoms have

[12] Phil. Mag., 40, pp. 472–88 (1920); 40, pp. 809–24 (1920).
[13] Astrophys. J., 55, pp. 119–44 (1922); 55, pp. 354–9 (1922).
[14] Observatory, 44, pp. 261–9 (1921).

electrons in the second orbit, sufficient to account for the reversal of Balmer lines such as H_α.

At great heights above the reversing layer, where the temperature is still high but the pressure is extremely low, simple ionization of elements having a fairly low ionization potential will be practically complete, as illustrated by Table XXVI. Accordingly while enhanced lines may be emitted, the arc spectrum of many of the elements should be absent in the high level chromosphere. Mitchell found from observation of the flash spectrum that the H and K enhanced lines of Ca extended to 14,000 km while the g arc line terminated at 5000 km. The ionization potential of Sr is lower than that of Ca and complete ionization will be produced at higher pressures or lower levels. The flash spectrum shows that the arc lines of Sr disappear before those of Ca. At pressures below 10^{-3} atmosphere, Na is completely ionized; in the chromosphere the D-lines reach only to 1200 km. The ionization potential of magnesium is the highest of the alkali earths and the arc lines are found at 7000 km.

Russell points out that the behavior of Sc, Ti, V, Fe, Mn, Cr, Co and Ni in the spot spectrum is intermediate to that of Ca and Zn and states, "It may be surmised that the ionization potentials for these metals lie between 6 and 9 volts, as Saha has suggested without specifying his reasons."

Stellar Spectra

The temperatures of stars are usually measured by observing the spectral distribution of their radiant energy, just as has been done with our sun, and comparing this with the black-body distribution computed by Planck's law. The temperature of a black body for which the relative spectral distribution most nearly fits a particular stellar distribution curve is considered as the temperature of the star. Wilsing and Scheiner[15] and others have made such observations through the visible spectrum for a large number of stars, and Coblentz,[16] using a spectroradiometric method, has been able to extend the data from the ultra-violet to the far infra-red. It is evident from what has been discussed in the present chapter that a systematic correlation of the stellar spectra also permits the assignment of temperatures. This will be considered more fully in the following paragraphs, but to anticipate, we may state that such computations agree fairly well with the temperatures determined

[15] Wilsing, Scheiner and Munch, Pub. Astrophys. Obs. Potsdam, Vol. 24, No. 74, 1920.
[16] Bur. Standards Sci. Paper No. 438.

from the black-body distribution without reference to spectral lines. This is illustrated by Table XXXI, in which the data of Saha were obtained by the degree of ionization method. In general the P stars are the hottest with a continuous decrease in temperature in the order P, O, B, A, F, G, K, M, N to R.

TABLE XXXI

RANGE OF STELLAR TEMPERATURES

Stellar Class	Typical Star	Wilsing & Scheiner and others	Coblentz	Saha	Remarks
Pb......	Great Orion Nebula	15000	—	—	
Pc......	I. C. 4997.........	30000	—	—	Gaseous nebulae with bright lines
Oa......	B. D. + 35°, 4013..	23000	—	23000	
Ob......	B. D. + 35°, 4001..	—	—	22000	Hereafter, all lines are dark
Bo......	ε Orionis...........	20000	13000	18000	
B 5 A...	*q* Tauri............	14000	—	14000	
Ao......	α Canis Majoris....	11000	8000	12000	
A 5 F...	β Trianguli........	9000	—	—	
Fo......	α Carinae..........	7500	—	9000	
F 5 A...	α Canis Minor.....	7200	6000	—	
Go.....	α Aurigae..........	7100	6000	7000	The sun is a dwarf star of this class
G 5 K...	α Reticuli..........	4500	—	—	
Ko.....	α Bootis...........	3700	4000	—	
K 5 M..	α Tauri...........	3500	3500	—	
Ma.....	α Orionis..........	3000	3000	5000	
Md.....	*O* Ceti............	2950	—	4000	
N, R.....		2300	—	—	

Table XXXII, taken from Saha's paper, is a compilation of the intensity of several typical lines appearing in stellar spectra. Lines which are barely visible are assigned the numeral 1. The symbol ⊕

TABLE XXXII

TYPICAL STELLAR SPECTRA

Element	He			He$^+$			H	Ca	Ca$^+$	Mg$^+$
Line	4471	4713	4386	4686	4542	4860	4860	4227 (g)	3934 (K)	4481
Notation	$2p-4d$	$2p-4s$	$2P-5D$	$4N\left(\frac{1}{3^2}-\frac{1}{4^2}\right)$	$4N\left(\frac{1}{4^2}-\frac{1}{9^2}\right)$	$4N\left(\frac{1}{4^2}-\frac{1}{8^2}\right)$	$N\left(\frac{1}{2^2}-\frac{1}{4^2}\right)$	$1S-2P$	$1\mathfrak{S}-2\mathfrak{P}_1$	$3\mathfrak{D}-4\mathfrak{B}$
Stellar Class										
Pe	—	—	—	⊕	⊕	—	—	—	—	—
Pf	—	—	—	⊕	⊕	⊕	—	—	—	—
Oa	0	—	—	⊕	⊕	⊕	—	—	—	—
Ob	0	—	—	100	12	10	0	—	—	—
Oc	1	—	—	40	3	3	0	—	—	faint
Od	1	—	—	20	10	20	10	—	2	faint
Oe	15	2	3	8	5	25	10	—	2	1
Oe 5	15	4	5	5	4	25	20	—	5	1
Bo	15	5	6	2	2	25	25	—	3	2
B 2	22	6	10	1	0	35	35	—	4	3
B 3	22	6	10	0	0	40	40	—	4	4
B 5	10	3	7	—	—	—	60	—	8	7
B 8	5	1	3	—	—	—	80	faint	⊕	7 (?)
B 9	4	0	1	—	—	—	90	faint	⊕	7
A 0	0	—	0	—	—	—	100	2	10	10
A 2	—	—	—	—	—	—	100	4	40	15
A 3	—	—	—	—	—	—	90	⊕	70	⊕
A 5	—	—	—	—	—	—	70	⊕	80	⊕
F 0	—	—	—	—	—	—	50	⊕	120	⊕
F 5	—	—	—	—	—	—	40	15	150 (?)	faint
Go	—	—	—	—	—	—	20	20	200	faint
G 5	—	—	—	—	—	—	15	⊕	200 (?)	0
Ko	—	—	—	—	—	—	10	60	150 (?)	0
K 5	—	—	—	—	—	—	5	⊕	⊕	—
Ma	—	—	—	—	—	—	2	⊕	⊕	—
Mb	—	—	—	—	—	—	—	100	faint	—
Mc	—	—	—	—	—	—	0	strong	faint	—
Md	—	—	—	—	—	—	—	strong	0	—

denotes a line the intensity of which cannot be obtained from the Harvard Annals. An interrogation point (?) denotes that the intensity is not stated in numbers in the Harvard Annals but is compiled from scattered descriptions. The symbol M^+ denotes that the line is due to the simply ionized atom of the element M. This table shows that the lines of an element begin to appear at a certain stage, rise step by step to a maximum and disappear at the other end of the scale. Thus hydrogen λ 4860, a line of the neutral atom, begins to appear in the low temperature Ma stars, reaches a maximum in the hotter A group and fades out as the temperature increases, finally vanishing at Oc where the temperature is sufficient to ionize hydrogen completely. In low temperature stars the arc spectrum of calcium is prominent. As we progress to stars of higher temperature, spark lines appear, arising in ionized atoms. Further increase in temperature increases the proportion of doubly ionized atoms and initiates the process of triple ionization. The arc lines vanish because neutral atoms are no longer present. Finally the spark lines fade out, giving place to enhanced lines of the second type, the identification of which is yet to be made. A similar development may be carried through for lines of other elements.

From a consideration of the degree of ionization of the elements, a table may be prepared showing the characteristic spectra which may be expected as the temperature increases. Saha has pointed out several striking phenomena in this manner, which are briefly summarized in Table XXXIII. It is evident from this table that a star which shows lines of ionized helium, for example, must have a very high temperature. The new field which Saha has opened appears to offer great possibilities in the realm of astrophysics. At present however the subject is in only the earliest stage of development, and as Russell states, it will require years of work to correlate systematically the numerous variables involved.

TABLE XXXIII

Important Steps in Thermal Ionization

Phenomena	Stellar Class	Temperature	Remarks
Appearance of the K line	Mc	4,000 K	Beginning of the ionization of Ca
Disappearance of the g line	B 8 A	13,000	Ca completely ionized
Appearance of Mg^+ 4481	Go	7,000	Mg considerably ionized
Disappearance of the K line	Oc	20,000	Ca^+ completely ionized
Mg^+ 4481 disappears	Oa	23,000	Mg^+ completely ionized
Appearance of 4686	B 2 A	17,000	He considerably ionized
Disappearance of 4471	Oa	24,000 (10^{-1} atm.)	He completely ionized
Appearance of Balmer lines	Mb	4,500	Appearance of the 2-quantum orbits of H
Appearance of He lines	Ao	12,000	Appearance of 2-quantum orbits of He
Maximum absorption of hydrogen lines	Ao	12,000	Maximum concentration of 2-quantum orbits of H
Maximum absorption of helium lines	B 2 A	17,000	Maximum concentration of 2-quantum orbits of He
Disappearance of 4295	B 8 A	14,000 (10^{-1} atm.)	Sr^+ completely ionized
Disappearance of Balmer hydrogen lines	Ob	22,000	H completely ionized
Disappearance of 4686	Pe	25,000–30,000	He^+ completely ionized

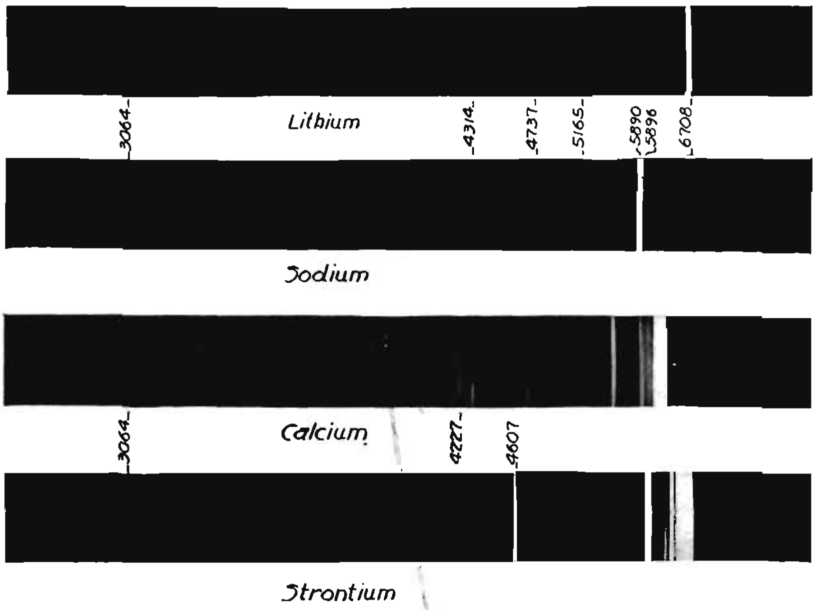


Fig 28A. Bunsen flame spectra. Swan spectrum, CO, 4314, 4737, 5165 A. Wat vapor, H_2O, 3064 A. Li, 6708; Na, 5890, 5896; Ca, 4227; Sr, 4607 A. Banc in yellow and red due to CaO and SrO.

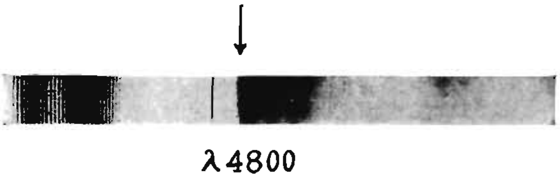


Fig. 29. Emission spectrum of iodine.

Chapter VIII

Thermochemical Relations

Electron Affinity of Atoms

We have mentioned in the latter part of Chapter IV that excited atoms may possess an electron affinity, tending to pick up an electron and become negative ions. This is also true of many diatomic molecules in the normal state, and on page 76 we showed that the Bohr hydrogen molecule leads to a value of 1.6 volts for its electron affinity. That is, work equivalent to 1.6 volts must be done on the negative molecular ion to reduce it to the normal molecular state.

Certain normal atoms, particularly the halogens, are known to possess an attraction for electrons. An atom of a halogen gas has an outer shell containing seven electrons. We have seen that there is a general tendency for electrons to be grouped in pairs or octets, as such a grouping represents a high degree of stability. The halogen atom tends to pick up an extra electron, completing its outer shell of eight. As a negative ion it resembles the stable rare gases in structure. It is this tendency, for example, for the normal chlorine atom to complete its outer shell, which enables it to attract the valence electron of sodium and form the compound NaCl. If a chlorine atom captures an electron and thus becomes a negative ion, work must be done on the ion to reduce it to the neutral condition. This work may be expressed in volts per atom or in calories per gram atom, the latter referring to the work which must be done to reduce 1 gram atom of the gas (*i.e.* 6.06×10^{23} negative atom-ions) to neutral atoms.

Franck[1] in a very suggestive paper has recently opened a new field connecting electron affinity with spectroscopic phenomena. The system neutral halogen atom and a stationary electron just outside the atom represents the *initial* quantized state on the Bohr conception. The final state is that of the atom-ion with its outer shell of eight electrons. If the electron falls directly from the initial state of energy W_i to the

[1]Z. Physik, 5, pp. 428–32 (1921).

final state of energy W_f the system loses an amount of energy $W_i - W_f$. This is assumed to be radiated as a single quantum of wave number ν_0 so that $W_i - W_f = hc\nu_0$. Since $W_i - W_f$ represents the work which must be done upon the atom-ion to reduce it to a normal atom, the radiated light of wave number ν_0 is a direct measure of the electron affinity E. The question as to whether intermediate quantized states may exist between the initial and final configuration may be of little importance. If intermediate states do exist they may not differ materially from the initial state since the field in the neighborhood of a neutral atom must decrease with a high power of the distance. Hence we should have a spectral series, the first line of which is nearly as short a wave-length as its convergence. The entire series should lie in an extremely narrow spectral region which for the present may be considered a single line.

This line of wave number ν_0 is emitted only in case an electron of zero velocity is captured. However, the atom may attach to itself an electron which initially is speeding toward it with a velocity v. Possibly the range of initial velocities may not be large. An electron of velocity greater than that corresponding to the electron affinity might penetrate the atom and escape. If, however, for a small range of the velocity v the atom captures the electron, the energy of the system will be altered from $W_i + \frac{1}{2}mv^2$, initial, to W_f, final, and the resulting radiation will be given by the equation:

$$hc\nu = W_i - W_f + \tfrac{1}{2}mv^2 = hc\nu_0 + \tfrac{1}{2}mv^2. \qquad (128)$$

Since the term $\frac{1}{2}mv^2$ may assume any value equal to or greater than zero, with possibly certain restrictions above mentioned, the emitted radiation is a continuous spectrum with a sharp limit on the *long* wave-length side corresponding to $v = 0$, and with gradually decreasing intensity toward the short wave-length side representing a decreasing probability of the capture of high velocity electrons by the atoms.

Figure 29 shows a spectrogram, made by Steubing,[2] of the emission spectrum of iodine. We find a region of bright continuous emission sharply defined on the long wave-length side at λ 4800 $\pm$ 15. Higher resolution showed that this was perfectly continuous and did not possess structure characteristic of ordinary band spectra. The continuous radiation was shown to be emitted by the atom rather than by the molecule. This was indicated by certain tests in a magnetic field and by the fact that it increased in intensity when the vapor was heated to a

[2] Ann. Physik, 64, pp. 673–92 (1921).

point where, at the pressure employed, the greater part of the iodine must have been dissociated.

Using for ν_0 the wave number corresponding to the observed limit λ 4800, one computes for the electron affinity of iodine a value 2.57 volts per atom or 59.2 kg. cal. per gram atom. This is in only fair agreement with determinations by less precise means. Unfortunately in this new field satisfactory spectroscopic data are not as yet available for other elements.

In Table XXXIV is a summary of determinations of electron affinity of several elements by the spectroscopic method just described and by two other methods discussed in the following sections.

TABLE XXXIV

ELECTRON AFFINITY

Method	Spectroscopic		Grating Energy		Ionization	
Element	volts/atom	kg.cal./g atom	volts/atom	kg.cal./g atom	volts/atom	kg.cal./g atom
Cl^-.......			5.0	116	4.8	110
Br^-.......			3.8	87	3.1	71
I^-........	2.57	59.2	3.5	81	2.8	64
S^{--}.......			2.0	45		

GRATING ENERGY, IONIZATION POTENTIAL AND ELECTRON AFFINITY

On the assumption that in addition to the ordinary Coulomb force of repulsion or attraction between the charges on the ions forming the crystal structure of certain salts, there exists between two ions a repulsive force,[3] the potential of which is inversely proportional to the nth power of the distance apart, Born[4] has computed the grating energy of various crystals. This is the amount of work U necessary to convert 1 mol of the crystal into free positive and negative ions, and its computation is purely an electrostatic problem. The value of the exponent n depends upon the form of the lattice space, as determined by x-ray analysis, and upon other physical constants. For most of the alkali halides $n = 9$. To discuss the assumptions here involved or to enter into a consideration of the details of the problem is beyond the scope of

[3] This force represents, as an approximation, the electrostatic fields due to the outer electrons of the atoms.

[4] Verh. Physik. Ges., 21, pp. 13–24 (1919); 21, pp. 679–85 (1919).

this book. Suffice to say that determinations of *grating* energies have yielded results of the greatest importance in many fields of physics and chemistry. We shall indicate here in the most elementary manner how spectroscopy is involved, through electron affinity and ionization potential, in grating energies.

Let us consider a salt of the form RX where R is an alkali and X a halogen atom. All heat and work units are expressed in kg. cal.

Let

[ ] denote solid phase or crystalline state.

( ) denote gaseous phase.

D = heat of dissociation of $\frac{1}{2}$ gram mol (1 gram atom) halogen gas into monatomic gas.

S = heat of sublimation at absolute zero of 1 gram mol metal or salt.

Q = heat of formation of the salt from the elements in the ordinary state.

J = Work in kg. cal. necessary to ionize 1 gram mol salt or metal.

E = Electron affinity of 1 gram atom halogen gas, expressed in kg. cal.

E^- = 1 gm. mol of electron gas.

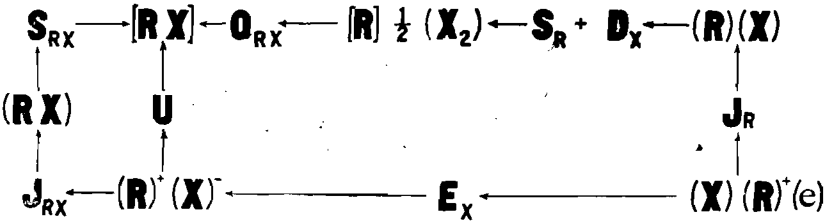


FIG. 30. Dissociation of the salt RX.

We shall consider the process in which the initial state contains ionized vapor atoms of the metal and negatively charged vapor atoms of the halogen gas, and in which the *final* state represents the solid crystal. The difference in total energies for these two states referred to a gram mol of the crystal is the grating energy U which Born computes from purely electrostatic and geometric considerations of the space grating. Physically the transition between the two states may be made according to the two schemes shown in Figure 30. We shall start with $(R)^+$ $(X)^-$ and go to the right. Traveling against the arrow,

work must be done; with the arrow, the reaction gives out energy. The first step requires an expenditure of the work E_X, resulting in a gram atom of neutral halogen atoms, positively charged metal atoms and electrons. The electrons are allowed to combine with the ionized metal atoms, giving up the energy J_R, the ionization potential in heat units, and producing a gram atom of monatomic halogen gas and a gram atom of the metal gas. In the next step we allow the metal gas to condense, giving up the heat of sublimation S_R, and the halogen atoms to combine into diatomic molecules, giving up the energy of dissociation D_X. The product is 1 mol solid metal and $\frac{1}{2}$ mol molecular halogen gas. These now combine into the solid crystal, giving up the heat of formation. Of course the reaction need not proceed in exactly this order. The step involving Q_{RX} is introduced because this is the quantity the chemist measures in determining heats of formation.

Another method of transition between the initial and final states is shown on the left of the figure. This probably more nearly represents the true physical process. The positive metal ion and the negative halogen ion react, forming the gas (RX) and give up the heat represented by the ionization potential[5] of this molecular gas. The gas is then condensed to the crystal state, during which process it gives up its heat of sublimation.

From the above considerations we may write at once the following thermochemical relations

$$U = J_{RX} + S_{RX} \tag{129}$$

and

$$U = -E_X + J_R + D_X + S_R + Q_{RX}. \tag{130}$$

Hence knowing the grating energy U and the heat of sublimation of the salt, it is possible to compute the ionization potential of the salt from Equation (129). Equation (130) gives a value of the electron affinity, which as discussed above determines the long wave-length limit of the continuous spectrum of the halogen. Eliminating U from the two equations, we obtain an expression for the ionization potential of the salt involving important physical and chemical constants. Unfortunately for the salts RX neither the ionization potentials nor the heats of sublimation are known. It is doubtful if the former may be determined at all by the ordinary methods of measurement. The heated vapor appears to dissociate very readily with temperature alone,

[5] Theoretically other types of ionization may exist as discussed later. In the example under consideration, however, ionization of RX in the vapor state without doubt produces dissociation as here assumed. For the present, if there be any question, we may consider this to be a *definition* of J_{RX}.

completely masking any ionization by electronic impact. The chemical data involved in Equation (130) are not known with a *high* degree of accuracy, but it is of interest to compute the electron affinity of several halogens, using what meager data exist. Equation (130) may be solved directly for E_X and the experimentally determined values substituted for the various constants or we may obtain the same result by considering in Table XXXV each separate step in the reaction illustrated by Figure 30. For the relation between volts/molecule and kg. calories/mol, refer to Equation (70). We shall first consider the salts KCl, KBr and KI, all data being expressed in kg. calories/mol or gram atom.

TABLE XXXV

ELECTRON AFFINITY OF HALOGENS FROM GRATING ENERGIES

Reaction	Cl	Br	I	Remarks
$[KX] = (K)^+ + (X)^-$	− 163	− 155	− 144	Born's grating energies.
$[K] + \frac{1}{2}(X_2) = [KX]$	+ 106	+ 99	+ 87	Heat of formation: cf. Fajans, Verh. d. Phys. Ges., 21, p. 716, 1919.
$(X) = \frac{1}{2}(X_2)$	+ 53	+ 23	+ 18	Heat of dissociation: cf. Fajans, *idem.*
$(K) = [K]$	+ 21	+ 21	+ 21	Heat of sublimation, from vapor pressure curve.
$(K)^+ + E^- = (K)$	+ 99	+ 99	+ 99	Ionization potential, Table X, $\nu = 1s$.
$(X) + E^- = (X)^-$	+ 116	+ 87	+ 81	Electron affinity, kg. cal./gram, atom.
	5.0	3.8	3.5	Expressed in volts/atom.
	2440	3350	3490	Expressed in Angstroms.

Of these three halogens we see that chlorine possesses the highest electron affinity. A similar set of results may be obtained from a consideration of other alkali halogen compounds. Equation (130) may be employed directly in the following manner, using chlorine as an example

$$E_{Cl} = -U_{KCl} + J_K + D_{Cl} + S_K + Q_{KCl}$$
$$= -163 + 99 + 53 + 21 + 106 = 116 \text{ kg. cal./gram atom.}$$

It is noted that the value obtained from the grating energy for the electron affinity of iodine is not in close agreement with that found by Franck by the direct optical method. Part of this discrepancy may be due to the inaccurate chemical data involved, but Born[6] is inclined to attribute it to the computation of the grating energy. Little is known of the existence of the repulsive force between the atoms in the crystal, and it is likely that the resulting potential energy cannot be represented by a single term of the form br^{-n}, an additional correction term being necessary.

The grating theory has been applied to other types of compounds. For example Born and Bormann[7] have used it to compute the electron affinity of the sulphur atom. The sulphur atom has an outer shell containing six electrons. In order to form the stable configuration of eight, it possesses a tendency to attract two electrons. It may therefore capture the two valence electrons of a zinc atom, forming the compound ZnS. The zinc atom in this union is doubly ionized, while the sulphur ion possesses a negative charge of two units. Table XXXVI represents the successive stages in the decomposition of this compound.

TABLE XXXVI

ELECTRON AFFINITY OF SULPHUR FROM GRATING ENERGY OF ZnS

Reaction	Heat	Remarks
$[ZnS] = (Zn)^{++} + (S)^{--}$	− 753	Grating energy of crystal, computed by Born and Bormann and later corrected by Born.
$(Zn) = [Zn]$	+ 28	Heat of sublimation obtained from vapor pressure data and other data; cf. Born.
$\frac{1}{2}(S_2) = [S]$	+ 14	Heat of sublimation to diatomic vapor (Pollitzer).
$(S) = \frac{1}{2}(S_2)$	+ 52	Heat of dissociation (Budde).
$[Zn] + [S] = [ZnS]$	+ 41	Heat of formation from metallic Zn and rhombic S (Mixter).
$(Zn)^{++} + 2E^- = (Zn)$	+ 663	From ionization potential Table XI and work required to remove 2d electron, Table XX, *i.e.* $(1S + 1\mathfrak{S})$.
$(S) + 2E^- = (S)^{--}$	+ 45	kg. cal./gram atom = E_S = electron affinity for two electrons.
	2.0	expressed in volts/atom.

[6] Born and Gerlach, Z. Physik, 5, pp. 433–41 (1921).
[7] Z. Physik, 1, pp. 250–55 (1920).

The electron affinity of the sulphur atom for two electrons is accordingly 2.0 volts/atom or 45 kg. cal./gram atom, a value which will be used in the following section.

Ionization of Vapors of Compounds

The simple ionization of a compound molecule, R_1X_1, may result in the following end products:

(a) a positive molecular ion $(RX)^+$ and an electron.

(b) a positive atom ion $(R)^+$, a neutral atom X, and an electron.

(c) a positive atom ion $(R)^+$, and a negative atom ion $(X)^-$.

In the association of these products of decomposition and the formation of the original molecule, radiation should be produced, but practically nothing either of a theoretical or experimental nature has been contributed to this phase of spectroscopy. A material ionizing according to (a) may possess an ordinary series line spectrum, an example of which may be CO. This molecule gives a definite line emission spectrum, but one which has not been correlated in series. Materials ionizing according to (b) or (c), besides emitting any radiation characteristic of association, should show the line spectrum of the component R. The former type of radiation has not been identified as yet, but the latter is very commonly observed. For example, the oxy-gas flame fed with NaCl shows the arc lines of sodium. The molecule is dissociated in the flame and the positively charged sodium atom picks up a free electron instead of the negative chlorine atom. Union of the electron and sodium ion gives rise to the arc spectrum of sodium. The sodium flame emission is known to be suppressed by an excess of chlorine. This is due to the fact that with a large number of chlorine ions present, the chance of a collision between the positive sodium ion and the negative chlorine ion is increased and the number of free electrons is reduced because of the electron affinity of the chlorine atom and its tendency to capture a free electron. Hence *relatively* more combinations of the type $Na^+ + Cl^-$ take place than of the type $Na^+ + E^-$, with the resulting decrease in intensity of emission of sodium lines. Hydrogen chloride in a spark discharge shows the spectrum of hydrogen which is produced in the above described manner.

The ionization of a molecule of the type R_rX_x is still more compli-

cated and nothing whatever is known of the spectroscopic relations. In the case of $ZnCl_2$, for example, the following may result:

(a) $(ZnCl_2)^+$ and an electron

(b) $(ZnCl)^+$ and $(Cl)^-$ or (Cl) and an electron.

(c) $(Zn)^{++}$ and 2 $(Cl)^-$ etc.

The second type of ionization appears very likely in low voltage discharge. The two negative chlorine ions are probably joined to opposite sides of the doubly charged zinc atom, and one of these may be ejected by a single electronic impact. Even though such compounds as ZnCl are incapable of stable existence, there is no apparent reason why they may not exist momentarily as a product of decomposition, and especially so as positive ions. In fact the existence of $ZnCl^+$ is recognized in electrolytic dissociation.

Lohmeyer[8] has studied the emission spectra of the mercury halides HgCl and $HgCl_2$. Each shows a characteristic complicated band structure, and it is possible that these will be interpreted after a careful consideration of the thermochemical relations involved.

In certain cases enough chemical data are known to enable the prediction of the ionization potential for molecules of the type RX, assuming they are ionized by dissociation. As an example we shall consider HCl, HBr, and HI. For HCl we have

$$\begin{aligned} (HCl) + Q_{HCl} &= \tfrac{1}{2}(H_2) + \tfrac{1}{2}(Cl_2), \\ \tfrac{1}{2}(H_2) + D_H &= (H), \\ \tfrac{1}{2}(Cl_2) + D_{Cl} &= (Cl), \\ (H) + J_H &= (H)^+ + E^-, \\ (Cl) + E^- - E_{Cl} &= (Cl)^-, \\ \hline (HCl) + Q_{HCl} + D_H + D_{Cl} + J_H - E_{Cl} &= (H)^+ + (Cl)^-. \end{aligned} \tag{131}$$

The last five terms on the left give the work required to ionize by dissociation one mol of hydrogen chloride. Hence the ionization potential J_{HCl} of HCl vapor may be computed from the following equation

$$J_{HCl} = Q_{HCl} + D_H + D_{Cl} + J_H - E_{Cl}. \tag{132}$$

A similar relation holds for HBr and HI. Table XXXVII summarizes the thermochemical data involved and shows the close agreement between the computed and observed ionization potentials. We have

[8] Z. wiss. Phot., 4, p. 367 (1906).

used here the electron affinities determined from the grating energies, Table XXXIV. Hence the computed values may be in error by several tenth volts from this source alone. The value 13.7 volts for HCl was obtained by the authors while the other determinations are by Knipping.[9]

TABLE XXXVII

COMPUTED AND OBSERVED IONIZATION POTENTIALS OF HCl, HBr, AND HI

	HCl	HBr	HI	Remarks
Q_{HX}	22	12	1	From Landolt-Börnstein.
D_H	42	42	42	Heat of dissociation ½ gram mol H_2 (Langmuir).
D_X	57	23	18	Cl—Pier; Br—Bodenstein; I—Starck and Bodenstein.
J_H	312	312	312	Bohr 13.54 volts — confirmed by authors; cf. Table XV.
$-E_X$.....	− 116	− 87	− 81	From Born's grating theory; cf. Table XXXIV.
J_{HX}	317	302	292	Expressed in kg. cal./mol.
	13.7	13.1	12.7	Expressed in volts/molecule.
	{ 13.7 14.4	13.8	13.4	Observed values.

It is evident that one may use the observed values of the ionization potentials to compute the electron affinity of the three halogen gases. We accordingly obtain 4.8, 3.1, and 2.8 volts for Cl, Br and I atoms respectively. The value for iodine is closer to Franck's determination by the optical method than is Born's value obtained from grating energy. However, this may be accidental, as the experimental values of the ionization potential may be in error by 0.5 volt.

Born and Bormann[10] have computed the ionization potential of hydrogen sulphide from thermochemical considerations on the assumption that the molecule is dissociated into two positive hydrogen atoms and a doubly charged negative sulphur ion. While computations of this kind are necessary in considering energy relations, it does not follow

[9] Z. Physik, 7, pp. 328–40 (1921).
[10] Z. Physik, 1, pp. 250–55 (1920).

that this value of the ionization potential would be observed directly. In a low voltage arc it is possible that only one of the hydrogen atoms is readily ejected by a single impact. This would permit the temporary existence of the negative ion $(HS)^-$. If such an ion collided with another electron the second hydrogen atom could be ejected, producing $(S)^{--}$ and $(H)^+$. The computed ionization potential 31.8 volts should be accordingly the sum of these two observed ionization potentials. The thermochemical relations for complete dissociation are as follows:

$$(H_2S) + Q_{H_2S} = (H_2) + [S],$$
$$(H_2) + 2\,D_H = 2\,(H),$$
$$2\,(H) + 2\,J_H = 2\,(H)^+ + 2\,E^-,$$
$$[S] + S_S = (S),$$
$$2\,E^- + (S) - E_S = (S)^{--},$$

$$(H_2S) + Q_{H_2S} + 2\,D_H + 2\,J_H + S_S - E_S = 2\,(H)^+ + (S)^{--}, \quad (132)$$

$$\therefore J_{H_2S} = Q_{H_2S} + 2\,D_H + 2\,J_H + S_S - E_S \quad (133)$$
$$= 5 + 84 + 624 + 66 - 45$$
$$= 734 \text{ kg. cal./mol} = 31.8 \text{ volts/molecule.}$$

The authors have observed the ionization potential of $ZnCl_2$ as 12.9 volts. This can be shown from a consideration of the thermochemical relations to be far less than the value necessary for complete dissociation into $(Zn)^{++} + 2\,(Cl)^-$. Complete ionization of this compound, as noted earlier, is more likely a two stage process with the intermediary production of $(ZnCl)^-$. Table XXXVIII gives a summary of recent determinations of critical potentials in compound vapors.

It is of interest that with zinc ethyl we were unable to obtain the spectrum of zinc, indicating that double ionization with this material in our apparatus was improbable.

Critical Potentials and Radiation from Elements in the Polyatomic State

We have pointed out in Chapter III that the quantum relation $hc^2\nu = eV \cdot 10^8$ where V is a critical potential, cannot be safely employed for the computation of characteristic wave numbers for elements which are polyatomic in the vapor state. Of course, if by increasing the temperature of the vapor a sufficient proportion of the molecules are dissociated into atoms, the critical potentials are then identified with the atom and the quantum relation may hold. There still may be exceptions to this, however, with atoms possessing an electron affinity.

TABLE XXXVIII

RESONANCE AND IONIZATION POTENTIALS OF MOLECULAR COMPOUNDS

Molecule	Critical Potential		Investigator and Remarks
	Resonance	Ionization	
HCl.......		13.7 14.4	Foote and Mohler. Knipping.
HBr.......		13.8	Knipping.
HI.........		13.4	Knipping.
HCN......		15.5	Knipping.
$ZnCl_2$......		12.9	Foote and Mohler.
CO........	?	10.1 14.3	Foote and Mohler (two ionization potentials and inelastic impacts at 6.4, 12.3, 14.0, 19.7, 22.3, 25.2, 27.7 and 30.9 volts).
		15.0	Found and Stead, and Gossling.
H_2O.......	7.6?	13 ?	Foote and Mohler.
$HgCl_2$......		12.1	Foote and Mohler.
$Zn(C_2H_5)_2$..	7	12	Foote and Mohler.
$C_4H_{10}O$.....	6.6	13.6	Boucher*
C_6H_6.......	6.0	9.6	Boucher.
C_7H_8.......	6.2	8.5	Boucher.
C_8H_{10}......	6.5	10.0	Boucher.
$CHCl_3$.....	6.5	11.5	Boucher.

* Phys. Rev., 19, pp. 189–209 (1922).

For example, we have found a pronounced resonance potential in iodine at 2.34 volts. If this is due to the atom, by the simple quantum relation we should expect a line at λ 5300. This line should appear in a

low voltage arc and should show absorption when a long column of iodine is heated to a point where a considerable amount of dissociation is present. Efforts to detect this line as well as the corresponding line for arsenic vapor have been unsuccessful. Of course there are thousands of lines present in this region, but these belong to the complicated molecular band spectrum and disappear if the temperature is high and pressure low.

Assuming, in the critical potential measurements, that the electronic impacts occurred with dissociated molecules, it is quite likely that the velocity of the 2.34 volt electron is further increased on account of the electron affinity of the iodine atom. The total kinetic energy absorbed should then be not 2.3 volts but 2.3 + E. This might give rise to a resonance line at 2200 A or possibly a band terminating in this region. However we are confronted with the experimental fact that an electron of higher speed, say 6 volts, may suffer a velocity loss of 2.3 volts and *leave* the atom with a velocity of 3.7 volts. What becomes of the energy corresponding to this velocity loss of 2.3 volts?

Various facts indicate that with polyatomic elements the ordinarily observed critical potentials are usually characteristic of the molecule rather than the atom. Accordingly the observed resonance potential might represent the true resonance potential of the atom plus the work required to dissociate the molecule. Similarly the ordinarily observed ionization potential may represent the true ionization potential of the atom plus the work of dissociation of the molecule. Smyth and Compton[11] observed two ionization potentials in iodine, the lower one being very faint, and 1.4 volts less than the more pronounced critical velocity. The work required to dissociate the iodine molecule is 1.6 volts. This lower faint ionization appears to correspond to the 13.5 point for hydrogen and may be due to the atoms which have been dissociated by the hot cathode.

Still further the molecule may be dissociated by the impact at the observed resonance potential and the impacting electron may be drawn into one of the atoms on account of the electron affinity. The characteristic radiation should then be located in another part of the spectrum and might be a band, a line or a group of lines. If we consider the electron affinity of the molecule many other simple possibilities readily suggest themselves.

In practically all cases the resonance potentials of the polyatomic elements lead to wave-length values which lie in a region of strong band

[11] Phys. Rev., 16, pp. 501–13 (1920).

absorption. A discussion of the theory of band spectra, which in its present initial stage of development is summarized by Sommerfeld,[12] cannot be here entered upon. The theory indicates that the connection between absorbed energy of electronic impact and final radiation as band structure may be involved and remote. The absorbed energy is distributed between the quantized vibratory and rotational states of the molecule. Brandt,[13] using the photo-electric method of measuring resonance potentials, found for nitrogen some twenty inflections in the radiation curve (similar to Figure 25) between 7.5 and 8 volts. On the Lenz theory these might correspond to the same final but different initial momentary, vibratory and rotational quantized states of the molecule.

We call attention to the above facts to point out that one cannot use the method of critical potentials to predict new series in polyatomic elements, as the simple relations established for the metallic vapors no longer apply.

If the resonance potential of iodine is related to the work of dissociation, the complicated band spectrum may appear considerably below ionization. Experiments indicate that the reaction $2\,I \rightarrow I_2$ produces an emission of these bands. Wood[14] first showed that iodine vapor, heated in a quartz bulb, emitted the complicated band spectrum. The emission is better demonstrated by using a large graphite heater at 2000° C in the center of a glass bulb containing iodine at rather high pressure. Strong convection currents of the vapor are set up. The molecules stream from the bottom up the center, past the heater, where they are dissociated, and then flow down to the bottom, following the walls of the bulb. Above the heater and along the walls, especially in the upper part of the bulb where recombination is taking place, the yellowish-red illumination in the vapor is brilliant. There is no emission below the heater where the gas is in the diatomic state, nor along the heater where the dissociation is occurring.

It is certain that some types of band spectra may be excited by electronic impact at a voltage less than the ionization potential. Leon Bloch and E. Bloch[15] observed the positive bands of nitrogen at 12 volts and the negative bands at 21.5 volts. They accordingly attribute the positive bands to the neutral molecule and the negative bands to the molecule which has been simply ionized. Meggers and the authors[16]

[12] "Atombau," 3d Ed. (1922). See also Birge, Astrophys. J., 55, pp. 273–90 (1922).
[13] Z. Physik, 8, pp. 32–44 (1921).
[14] "Physical Optics," 2d Ed.
[15] Compt. rend., 173, pp. 225–7 (1921).
[16] Unpublished work of Jan., 1921.

investigated the emission spectrum of nitrogen in the presence of sodium vapor which was introduced in order that the ionization of the latter might increase the current. A discharge tube of the type illustrated by Figure 22 was employed. The positive band group of nitrogen appears at 7 volts as shown in Figure 31, and at 25 volts the negative group is intense. The range from 18 to 25 volts was not studied. The field recently opened in the experimental study of band spectra from the quantum theory standpoint has already yielded fruitful results and rapid development is assured within the next few years.

Chapter IX

X-ray Spectra

Introduction

The radiation phenomena considered in Chapters III, IV and V involve primarily the valence electrons of atoms. The corresponding phenomena for the electrons in inner atomic orbits will be considered in the present chapter.

X-ray frequencies are in general higher than those of arc and spark spectra since the electrons are closer to the nucleus. However, the spectrum range extends to much longer wave-lengths than the ordinarily observed x-ray spectra, and overlaps part of the arc and spark range. Measurements with the crystal grating spectrometer extend from $\lambda = 12$ A to $\lambda = .1$ A or in terms of ν/N from 70 to 9000. Measurements by indirect means indicate x-ray wave-lengths as long as 700 A or $\nu/N = 1.3$ and no definite limit in this direction is known at present.

A fundamental difference between x-ray phenomena and valence electron spectra is that the former change with increasing atomic number from element to element in a continuously progressive manner. This regular sequence is evident in Figures 36 and 37, showing the emission spectra of several elements on the same scale. The approximate law of this progression, as stated by Moseley, is that the square roots of corresponding frequencies are proportional to the atomic number. The physical basis for the regularity evidently involves a similar and unchanging configuration of electrons within the atom combined with the increasing nuclear field. We have derived in Chapter I a fairly accurate equation for $K\alpha$ on the basis of certain assumptions as to this configuration.

Besides the regular change in frequency of x-rays, there is also a periodic progression in the complexity of spectra as successive electron levels are added to the atom structure. With each rare gas a new electron level is completed and another x-ray series or group of series

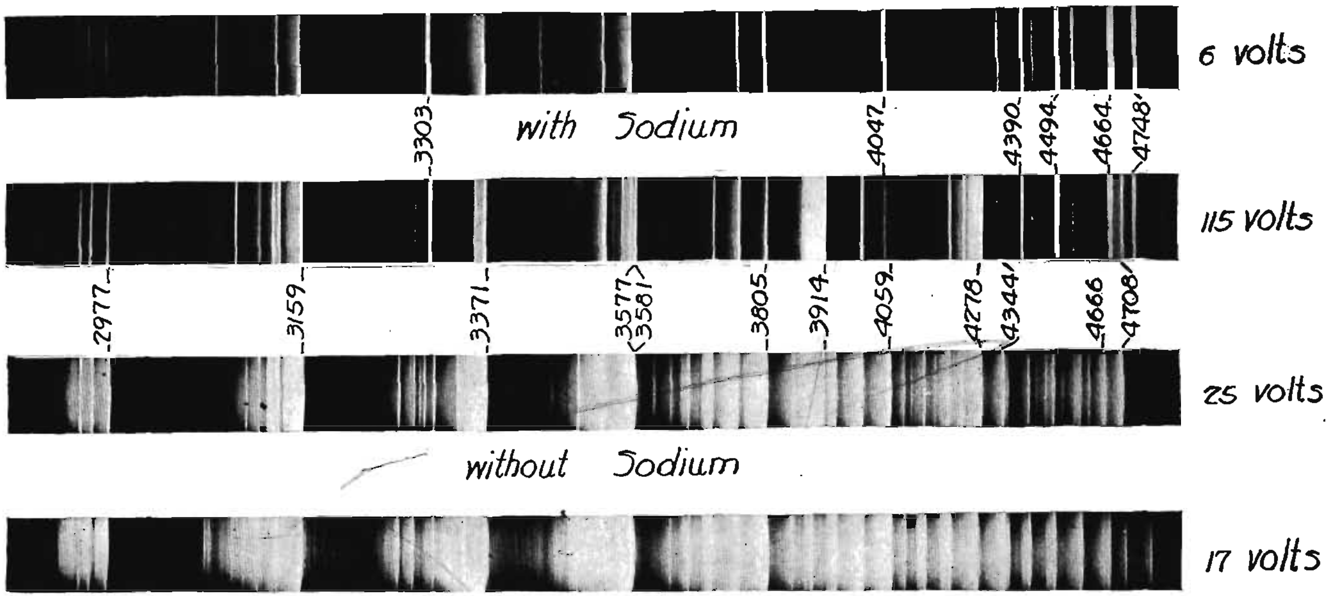


FIG. 31. Band spectra of nitrogen: 2d positive group 2977, 3159, 3371, 3577, 3805, 4059, 4344, 4666 A. Negative pole bands 3581, 3914, 4278, 4708A.

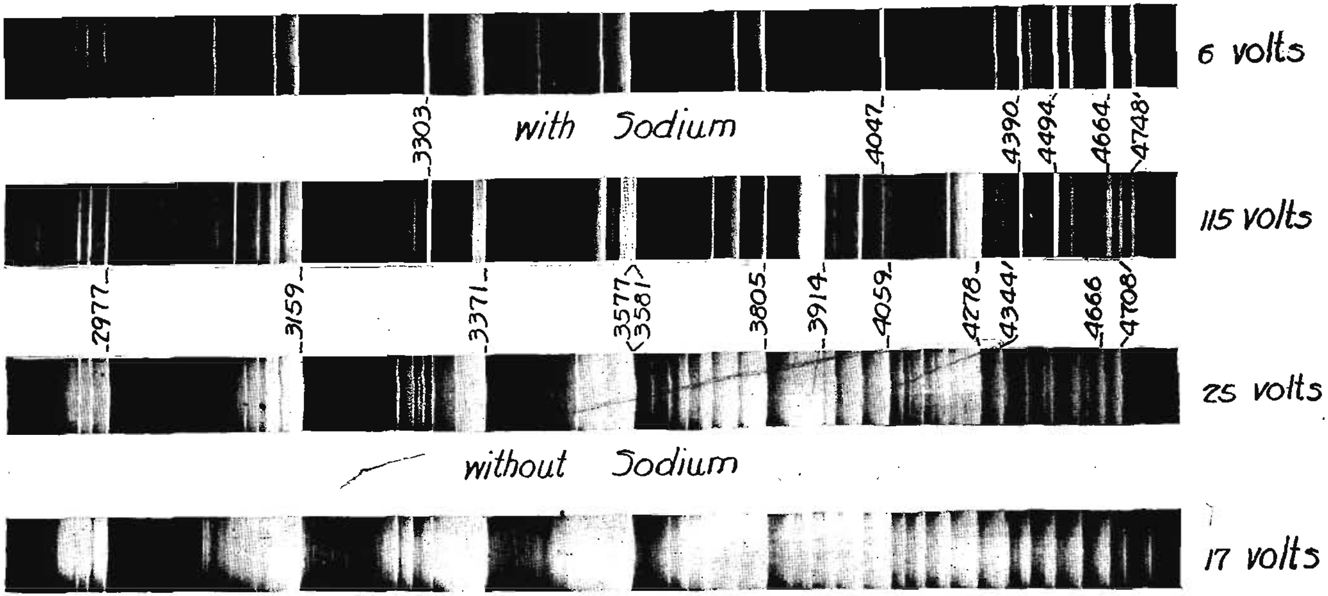


FIG. 31. Band spectra of nitrogen: 2d positive group 2977, 3159, 3371, 3577, 3805, 4059, 4344, 4666 A. Negative pole bands 3581, 3914, 4278, 4708A.

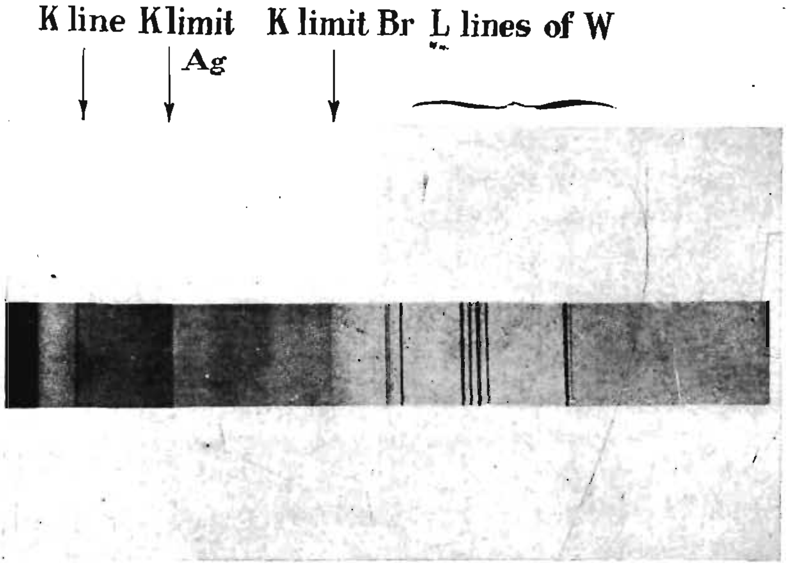


Fig. 32. Photograph by de Broglie, showing absorption bands of silver bromide superposed on the emission spectrum of tungsten.

AGRICULTURAL COLLEGE AND
LIBRARY
No.
10 JUN 1924
COIMBAT

begins. Table III, Chapter I, shows the order in which these levels appear in the periodic table. In the first row we have one inner level determining a *K* series; with neon a second level is completed and the *L* series starts. Similarly we assume that beyond argon, krypton, xenon and niton, we have the initiation of *M*, *N*, *O* and *P* series.

However, our knowledge of x-ray spectra is not as extensive as the above scheme would indicate. Spectroscopic data cover only the *K* series from sodium, $Z = 11$, the *L* series from zinc, $Z = 30$, and the *M* series from dysprosium, $Z = 66$. This range has been considerably extended by experimental methods independent of spectroscopic analysis as well as by combination relations of spectral lines, but *O* and *P* series remain largely hypothetical.

The phenomena of x-ray spectra will be considered under the subjects: (1) Critical potentials for x-ray excitation, (2) Absorption phenomena (including the transformations of absorbed energy), (3) Emission lines and the combination principle and (4) Theoretical significance of the system of absorption limits.

1. Critical Potentials for X-ray Excitation

An important difference between outer and inner atomic levels is that while there are outside of the atom various series of "virtual orbits" (positions of equilibrium unoccupied by electrons in the normal atom), within the atom all positions of equilibrium are normally filled. Hence the necessary condition for excitation of x-rays is the removal of an electron from the atom. Resonance potentials, single-line emission spectra and line absorption spectra, all of which involve removal of an electron to a virtual orbit, are absent or at least unobserved in *high frequency* phenomena.

Another distinction is that x-ray frequencies of an atom are independent of its chemical or physical state, for the reason that the energy levels of the inner structure are little affected by the outer electrons which are alone involved in chemical reactions.

The above statements need qualification. There is no sharp discontinuity between the principles involved in outer and inner atomic structure, but many factors, of importance near the surface, become negligible within the atom. The transition stage probably lies in the little known region between the ordinary ultra-violet and x-ray spectrum range.

The potential required to excite an x-ray series can be accurately

determined with the Coolidge tube. D. L. Webster and his associates[1] have observed critical potentials for several x-ray series. The method involves the measurement of the intensity of spectral lines at potentials slightly above the critical point and the extrapolation of the intensity-voltage curve to zero intensity. For the *K* series all lines start at one potential and above this point maintain their intensity ratios constant. Critical potentials thus measured agree within the experimental error[2] with limiting frequencies determined spectroscopically.

For the *L* series it was found that the lines occur in three groups starting at potentials corresponding to the three observed limiting frequencies. Four critical potentials have been distinguished in the *M* series of lead. The possibility of separately exciting the different groups of the *L* and *M* series is of fundamental importance in the interpretation of emission spectra.

It is evident that with sufficiently sensitive measurements of intensity it might be possible to measure critical potentials without resolving the radiation into a spectrum. X-ray limits should then appear simply as changes in slope in the total radiation-voltage curve. This method has been most useful in extending x-ray data beyond the range of the crystal grating.[3] Since all materials are opaque to radiation softer than ordinary x-rays, the radiation is detected by its photo-electric effect on electrodes within the x-ray bulb. In this manner the critical potentials required to excite the softest characteristic x-rays can be measured.

Table XXXIX summarizes the data on critical potentials obtained by this method. The results of the authors for nickel and tungsten and all values given by Kurth and other observers are from measurements of the radiation of solid anticathodes. The other potential measurements of the authors have been obtained from a study of radiation from a thermionic discharge in gas (or vapor) at low pressure. The radiation intensity from a gas is very much greater than from a solid target, at least in the low voltage range. It is essential to maintain conditions such that electrons receive their full speed before collision with the gas molecules (see description of experiments on low voltage excitation of arc and spark spectra; Chapter V, Figure 22). The photoelectric current per unit cathode current, for radiation either of a gas or solid, when plotted against applied voltage, gives a nearly straight line with change in slope at critical potentials.

[1] Reference 1 at end of chapter.
[2] See Chapter X.
[3] Reference 2 at end of chapter.

TABLE XXXIX

CRITICAL POTENTIALS AND CORRESPONDING FREQUENCIES OF SOFT X-RAYS

Element	Z	Data of Mohler and Foote		Data of Kurth		Series limit given by author
		Volts	ν/N	Volts	ν/N	
Beryllium....	4	116	8.57			*K*
Boron........	5	186	13.7			*K*
Carbon.......	6	272	20.0	290	21.4	*K*
				33	2.43	*L*
Nitrogen.....	7	374	27.6			*K*
Oxygen......	8	478	35.3	519	38.3	*K*
				50	3.68	*L*
Sodium......	11	35	2.58			*L*
		17	1.25			*L*
Magnesium...	12	46	3.40			*L*
		33	2.44			*L*
Aluminum....	13			123	9.11	*L*
Silicon.......	14			150	11.05	*L*
Phosphorous..	15	126	9.30			*L*
		110	8.13			*L*
		95	7.01			*L*
Sulphur......	16	152	11.2			*L*
		122	9.02			*L*
Chlorine......	17	198	14.6			*L*
		157	11.6			*L*
Potassium....	19	23	1.70			*M*
		19	1.40			*M*
Titanium.....	22			504	37.2	*L*
				145	10.7	*M*
Iron.........	26			757	55.9	*L*
				227	16.8	*M*
				50	3.69	*N* (?)
Nickel.......	28	80	5.91			*M*
Copper.......	29			1002	74.1	*L*
				297	21.9	*M*
				106	7.85	*N* (?)
Tungsten.....	74	60	4.42			*N*

Data of Other Observers		Volts	ν/N
Richardson and Bazzoni	Carbon *K*.....	286	21.1
	Molybdenum *M*.....	356	26.3
Hughes	Carbon *K*.....	215	15.9
	L.....	34.5	2.55
	Boron *K*.....	148	10.9
	L.....	24.5	1.81

Experiments with gases show that ionization takes place at the critical x-ray potentials. The increase in ionization is not as pronounced as the radiation change and in only two elements has it been studied, sodium and potassium.

It is seen from Table XXXIX that measurements of critical potentials cover nearly the entire interval between arc spectra and the range of the x-ray spectrometer. Most of the work has been concerned with light elements, as these furnish the safest starting point in the development of new methods.

The evidence that these radiation potentials are characteristic x-ray limits is found both in the agreement of observed potentials with limits computed from spectroscopic data (Figure 35), and in the Moseley relation between critical potentials and atomic number (Figures 34 and 35). The relation of these data to x-ray spectra will be considered in detail later. In the work with gases, x-radiation is superposed on arc and spark spectra. Many fainter potentials not listed in Table XXXIX were found, but it will require further study to classify them.

The results of Hughes are apparently inconsistent with those of other observers, and there is no evident explanation of the difference.

2. Absorption Phenomena

If a beam of continuous (heterochromatic) x-rays is passed through a thin layer of any element, spectroscopic analysis of the transmitted light shows a band absorption spectrum characteristic of that element. There is also a non-selective absorption, probably caused by pure scattering of radiation. Only the selective effect will be considered here. Figure 32 is a photograph of the emission of a tungsten anticathode in which the K absorption bands of the elements silver and bromine in the photographic plate are distinctly shown. The bands are regions of continuous absorption terminating abruptly on the low frequency side and fading out gradually with increasing frequency. The position of the sharp edge of each band coincides with a limiting frequency computed from critical potential measurements.

Energy absorbed in a band is expended in the ejection of an electron from the atom. Part of the absorbed energy is given to the atom and part to the electron. If $\bar{\nu}_1$ is the frequency of incident radiation and $\bar{\nu}_0$ a limiting frequency characteristic of the absorber, then an absorbed quantum of energy $h\bar{\nu}_1$ is expended:

(1) In work on the atom, $h\bar{\nu}_0$;

(2) In kinetic energy of the ejected electron;

$$\tfrac{1}{2} mv^2 = h\bar{\nu}_1 - h\bar{\nu}_0. \qquad (134)$$

This is identical in form with the equation originally proposed by Einstein to explain photo-electric phenomena of solids in the visible and ultra-violet regions.

One consequence of Equation (134) is that each absorption limit determines the least frequency which will eject an electron from the given level of the atom. Duane[4] has verified this very accurately for bromine and iodine. A beam of monochromatic x-rays was passed through an ionization chamber containing the vapor and the current measured for different frequencies. A sharp increase in the ionization was found at a frequency equal to the K limit.

The energy $h\bar{\nu}_0$ given to the atom is re-emitted as fluorescent radiation when the ionized atom recombines. It was known even before the days of x-ray spectroscopy that substances exposed to x-rays emitted a characteristic fluorescent radiation. As the excitation of an atom by radiation is identical, in its effect, with excitation by electron impact, viz. complete ejection of an electron from one of the inner atom levels, there is no need of any distinction between the resulting spectra.

The verification of Equation (134) requires the measurement of velocities of photo-electrons, ejected by radiation of a frequency greater than the absorption limit. The method of measurement developed by Rutherford and recently improved by M. de Broglie[5] is as follows. A thin layer of the material studied is placed in a narrow groove and illuminated by x-rays. A magnetic field parallel to the groove bends the photo-electrons into arcs of circles of radii proportional to their speed. This dispersed beam of electrons falls on a photographic plate giving a "corpuscular spectrum" in which the position of any image is a measure of the velocity of emission of a group of photo-electrons. If an element with absorption limits K, L and M were illuminated by x-rays of frequency $\bar{\nu}$, the resulting spectrum, with low dispersion, would consist of three lines corresponding to velocities v_1, v_2 and v_3 given by the equations

$$\left.\begin{aligned}\tfrac{1}{2}\, mv^2{}_1 &= h\bar{\nu} - K\\ \tfrac{1}{2}\, mv^2{}_2 &= h\bar{\nu} - L\\ \tfrac{1}{2}\, mv^2{}_3 &= h\bar{\nu} - M\end{aligned}\right\} \qquad (134a)$$

In practice, intense illumination is required so that a continuous x-ray spectrum is used rather than monochromatic radiation. The continuous spectrum of maximum frequency $\bar{\nu}$ then gives rise to a

[4] Reference 4 at end of chapter.
[5] Reference 3 at end of chapter.

"corpuscular spectrum" consisting of bands terminating sharply on the side of maximum velocity

$$\tfrac{1}{2} mv^2{}_1 \lesseqgtr (h\bar{\nu} - K) \qquad (134b)$$

etc.

The incident x-rays also excite characteristic fluorescent radiation in

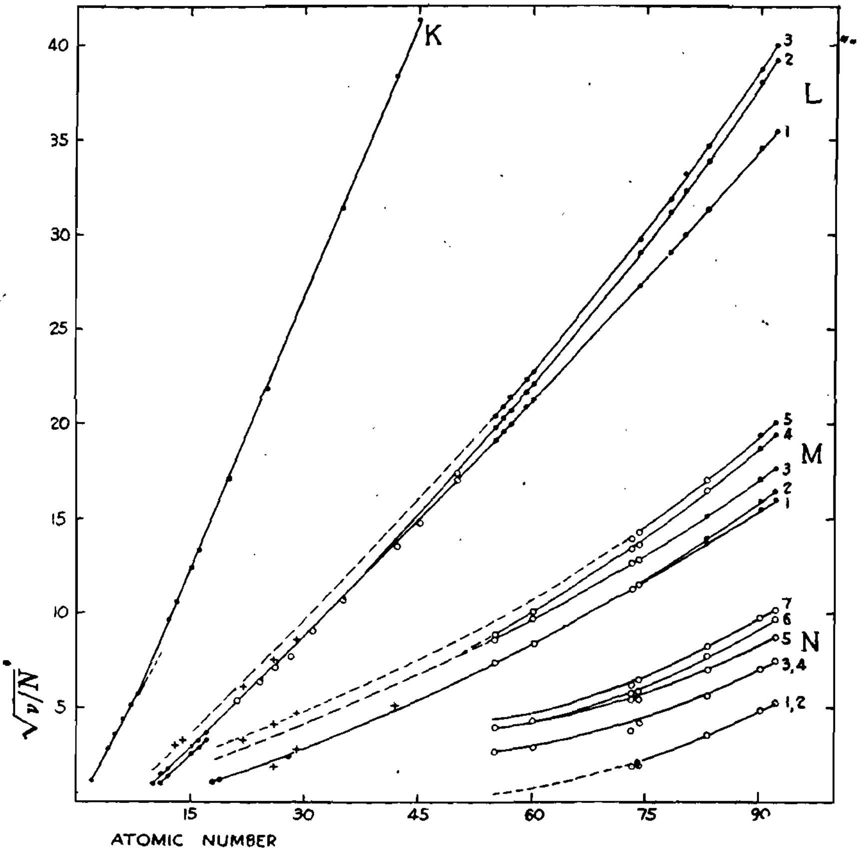


FIG. 33. Moseley diagram of absorption limits of the elements. Dots and crosses are limits observed spectroscopically and by potential measurements. Circles are values computed from emission spectra.

the material illuminated and these monochromatic rays give rise to a corpuscular line spectrum superposed on the band spectrum. Thus lines $K\alpha$, $K\beta$, $L\alpha$ and $L\beta$ of the fluorescent radiation produce electrons of velocities corresponding to frequencies $K\alpha - L$, $K\beta - L$, $K\alpha - M$, $K\beta - M$, $L\alpha - M$, $L\beta - M$.

De Broglie states that the corpuscular spectra can be measured with a precision comparable to spectroscopic methods. Evidently the method is not subject to the limitations of the crystal grating and in the future it may prove a very valuable means of studying atomic structure.

As absorption limits can be measured with a precision of .1 % or better through a wide spectrum range, they furnish our best means of measuring electron energy levels within the atom. De Broglie opened this field of research. The precision measurements of Duane and his associates, together with the work of Fricke, Stenstrom, Hertz, and others, furnish a basis for the classification and interpretation of all x-ray spectra.[6]

The K series absorption limits have been measured for nearly all elements from magnesium $Z = 12$ to uranium $Z = 92$. As critical potentials have been measured from beryllium $Z = 4$ to oxygen $Z = 8$, inclusive, our knowledge of the innermost energy levels of the elements is nearly complete. The K limit is in general observed as a single discontinuity in the continuous absorption.[7] Figures 33 and 34 show the K limits, for the light elements, plotted on the Moseley scale. The points all fall on a smooth curve which is nearly linear from magnesium to uranium. Between oxygen and magnesium there is a change in slope of this line. The ionization potential of helium at 25.5 volts has been included on these diagrams. It falls exactly on the extrapolated K line and is evidently the starting point of the series.

The K limit of uranium is of peculiar interest, as it is the upper limit of the range of atomic line-spectra. Duane's measurements give the following values $\lambda = .1075$ A; $\nu/N = 8{,}476$; critical potential 114,770 volts. Radiations of higher frequency than this exist. Some of the hard γ rays may be of very much shorter wave-length, but these are undoubtedly vibrations from within the nucleus. They are not strictly speaking characteristic of the 92 chemical elements but of the 200 or so different types of nuclei.

L absorption limits have been spectroscopically measured for elements $Z = 55$ to 92. Each of these elements shows three superposed bands, of which the long wave-length limit is strongest. These will be designated L 1, L 2 and L 3 in order of decreasing wave length.[8]

[6] Reference 4 at end of chapter.

[7] Absorption limits of long wave-length in this and other series show a fine structure at the edge of the band which will be discussed later.

[8] The notation K 1, L 1, etc., serves present purposes better than $K\alpha_1$, $L\alpha_1$, etc., used in former chapters. It avoids confusion with the line notation $K\alpha_1$, $L\alpha_1$, etc. Similarly M and N limits will be numbered in the order of their frequency, the lowest being 1.

L limits for ten light elements between sodium 11 and copper 29 can be computed from critical potential measurements. Here too the authors have observed several limits for each element, but the highest potential corresponds to the doublet *L* 1, 2 and the other limits are new series not found in heavy elements. Figure 35 gives the beginning of the *L* series and Figure 33 the entire series. The ionization potential of Neon at 16.7 volts falls on the line *L* 1, 2 and is assumed to be the beginning of the series.

M series limits have been observed spectroscopically only in uranium, thorium and bismuth. Five limits are known for the first two elements and three for bismuth. Four critical potentials have been measured for the *M* emission lines of lead and Table XXXIX gives potential measurements of *M* limits for five light elements. The limits ascribed by Kurth to the *N* series are probably *M* limits. Much of our knowledge of the *M* series and outer levels is derived indirectly from the data on emission lines. Detailed consideration of the relation of these critical potentials to the system of absorption limits will be given later.

In the above treatment of absorption phenomena we have assumed that the limits are single discontinuities in the continuous absorption. Stenstrom and Fricke[9] have obtained spectrograms with relatively high dispersion which indicate that this is not the case. Fricke describes the structure of soft *K* limits as a distinct boundary on the long wavelength side followed by an absorption line or band and sometimes by two bands. The interval between the boundary and first line varies from $\lambda = .002$ A to .01 A and indicates an energy difference between the levels of the line and boundary of from 2 to 25 volts.

Kossel[10] has suggested that this line absorption may be ascribed to the virtual orbits outside the atom. But if this is true, the boundary of the absorption cannot give the energy required to remove an electron from the atom, since the lines are of higher frequency than the limit. If the lines are so explained, the limit of the band may give the work required to displace a *K* electron to the incomplete valence ring. Fricke states that the structure observed is apparently not consistent with the above hypothesis. Another possible theory is that the lines are limits for multiply ionized atoms.

The potential measurements of the authors gave no evidence of a structure of this kind. In the case of potassium and sodium the principal radiation potentials agreed within experimental error (1 or 2 volts)

[9] Reference 4 at end of chapter.
[10] Reference 5 at end of chapter.

with ionization potentials for an x-ray level. This is probably the most direct evidence that x-ray absorption is accompanied by ionization

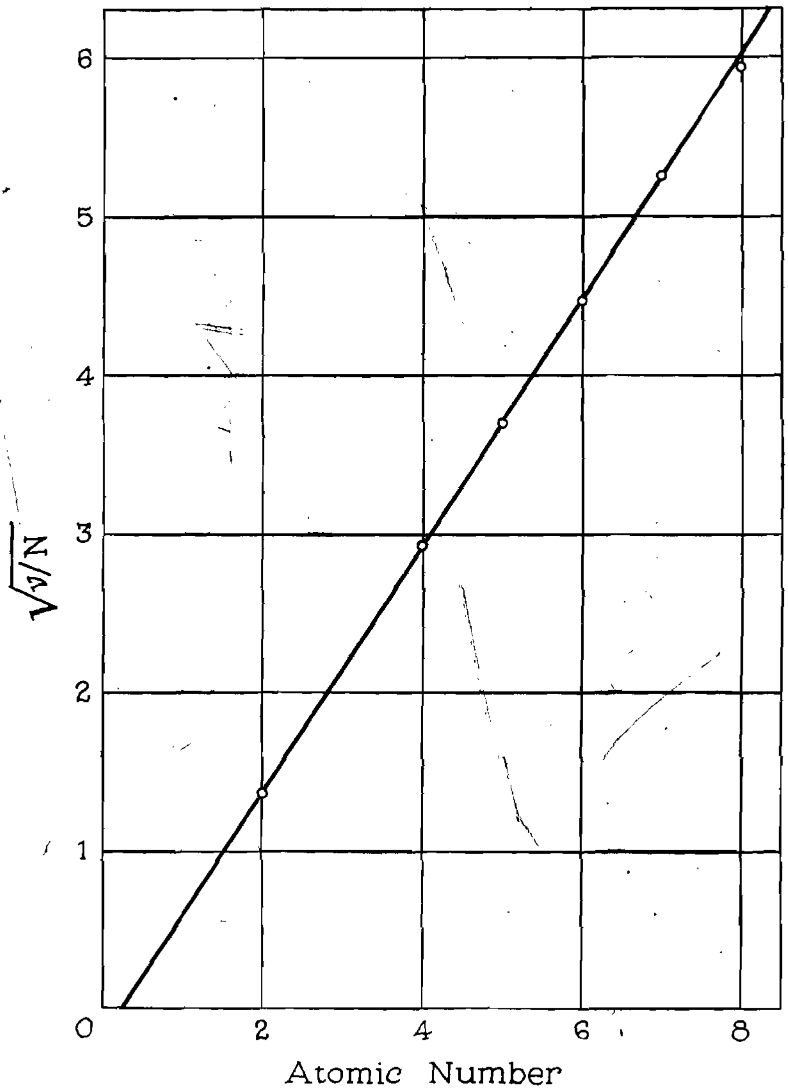


FIG. 34. *K* limits observed by the authors and the ionization potential of helium.

and that the absorption limit corresponds exactly to the work of ionization from an x-ray level. Our results, however, do not exclude the

possibility of excitation without ionization at other critical potentials. Some faint radiation potentials (not listed in Table XXXIX) were observed for elements of the first row, which may be in the future identified with potentials required for excitation of single line K spectra. It is probable that in the outer x-ray levels, the phenomena of line absorption and resonance spectra become of importance. With valence electrons, line absorption is the chief characteristic, and continuous absorption beyond the series limit very faint, while with high frequency spectra the second factor becomes predominant. In the intermediate range we should expect to find the transition, although conclusive experimental evidence of this is yet to be found.

It also may be predicted that limits of x-rays are not entirely independent of the chemical and physical state of an element. Indications of a difference in K limits of various compounds of phosphorus and chlorine have been observed.[11] On the other hand measured K limits of four carbon compounds showed no detectable difference[12] (less than 1 volt).

The possibility of locating absorption limits by measurements of the absorption coefficient of elements for radiation not resolved by the spectroscope, is shown by Holweck.[13] The continuous x-rays from a solid bombarded by thermions (electrons) are passed through screens of very thin celluloid and the absorption coefficient of gases and solids for the residual radiation is determined. Now the continuous radiation has a maximum wave number ν given by the applied potential V, viz. $\nu = 8100\ V$. If this radiation is passed through screens exhibiting only general absorption (no bands) in the region studied, the lower frequency radiation will be entirely absorbed and the transmitted fraction will become more homogeneous, approximating monochromatic light of wave number ν. This is known to be true in the range of x-ray spectra and Holweck, assuming it true at low voltage, was able to estimate the position of absorption bands from curves of total absorption vs. potential. Results are given in Table XL, together with comparison data from other sources. As the technique of the measurements is difficult, the agreement must be considered at present merely as a satisfactory check on results by other methods. A most important phase of Holweck's work is the study of the laws of non-selective absorption in the low voltage range. We cannot consider this subject here except to state that the results justify the fundamental assumptions of the method.

[11] Reference 6 at end of chapter.
[12] Reference 2 at end of chapter.
[13] Reference 7 at end of chapter.

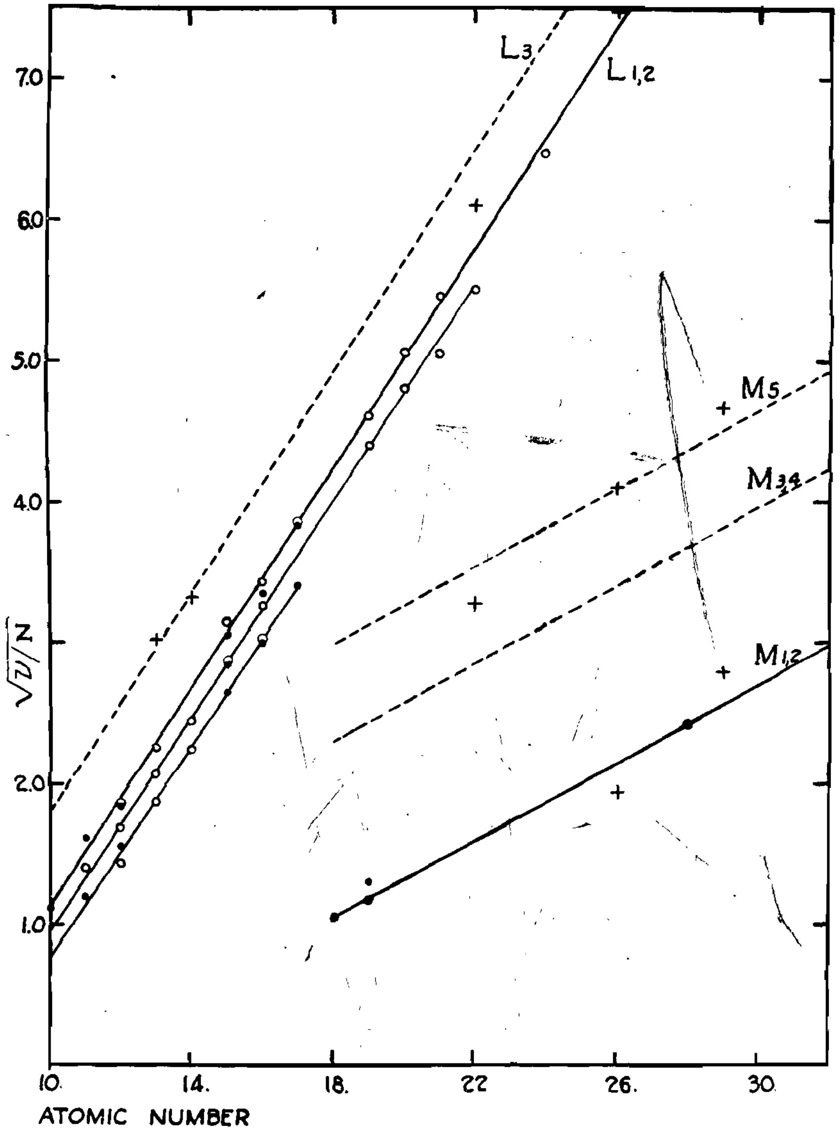


Fig. 35. Soft L and M limits. Dots and crosses give results of potential measurements. Circles are limits computed from K spectra.

TABLE XL

ABSORPTION LIMITS MEASURED BY HOLWECK

X-ray Limit	Volts	ν/N	Comparison Data	
Carbon K......	290 approx.	21.4	20.0	Mohler and Foote.
Aluminum L....	64 ± 2	4.7	4.8	Figure 35.
Aluminum K....	1555 ± 10	115.0	114.8	Fricke.
Boron K.......	160 approx.	11.8	13.7	Mohler and Foote.
Gold N 1, 2? ...	160 approx.	11.8	9	Figure 33.

3. EMISSION LINES AND THE COMBINATION PRINCIPLE

The first survey of the field of x-ray emission spectra was made by Moseley soon after the discovery of the crystal spectrometer by Bragg. Since that time rapid progress has been made in the precision and range of measurements and particularly in the discovery of new lines in known series.[14] Figures 36 and 37 show typical K and L photographs. Many more lines have been measured than can be seen in the reproduction, and the complexity, particularly of the L groups, is increasing with every improvement in technique. Measurements of line spectra have been extended to somewhat longer wave-lengths than absorption limits.

An interesting recent development is the extension of the range of the diffraction grating by Millikan.[15] He finds isolated groups of lines in the extreme ultra-violet spectra of sodium, magnesium and aluminum which he ascribes to their L series. The wave-lengths of the strongest of these are

Na–372.2 A, Mg–232.2 A, Al–144.3 A.

The above lines were designated as $L\alpha$, but for magnesium and aluminum the wave-lengths are shorter than the limit $L\,1$. A possible explanation of their origin which is consistent with other data will be given later. Similar groups of lines are found for elements in the first row of the periodic table. These are apparently related to the L limits of carbon and oxygen found by Kurth. Though the theoretical significance of these extreme ultra-violet emission spectra is as yet in doubt, they at least promise an important field for future research.

The extensive and accurate data on high frequency spectra furnish us the basis of our knowledge of the *inner* structure of the atom. An

[14] Reference 8 at end of chapter.

[15] Reference 9 at end of chapter.

important step in this study is the development of a combination principle[16] which relates emission lines and absorption limits in a manner analogous to the combinations found in arc or spark spectra. A system of combinations was first proposed by Kossel, but the complexity of absorption limits was not then known, and the scheme is too simple for a satisfactory interpretation of the spectra. In the past year several physicists have independently developed combination principles adequate for the explanation of nearly all observed emission lines.

The initial condition for x-ray emission is an electron deficiency in an inner atomic level. The emission of a spectrum line results when an electron from an outer orbit falls into the vacant place. The final state with respect to this process is accordingly an atom with an electron deficiency in a higher level and the process is then repeated until the atom assumes the normal state. The quantum radiated is equivalent to the difference in energy of the two successive states involved. The energy of each state, referred to the normal as zero, is proportional to a limiting frequency. Hence the frequency radiated should be equal to the difference of two absorption limits. The following pages give the experimental verification of this conclusion.

We shall consider in detail the x-ray spectra of tungsten consisting of the experimentally determined K limit, 3 L limits and over 30 emission lines, the ν/N values for which are listed in Table XLI. These spectroscopic data with a few exceptions are from a table by Smekal[17] and data of Duane.[18] The notation is that of Siegbahn as revised by Coster.[17] The system of combinations follows the scheme of Wentzel.[17]

In Figure 38 we have plotted as vertical lines the differences between absorption limits and emission lines. Thus in the lower row are plotted $K\,1 - K\alpha_1$, $K\,1 - K\alpha_2$, etc. This row of lines gives according to the combination principle the energy levels involved in K emission lines. The origin is the atom surface. The observed L limits plotted in the second row are seen to agree with the computed values. For convenience L and M series are plotted on a larger scale.

In the computation of a limit from an L line we must first determine which of the three L limits corresponds to the initial state. Experiments by Hoyt[19] on the critical potentials of tungsten give the series limits of a number of the lines (designated by * in Table XLI) and the remaining lines are classified so that they are consistent with those of

[16] Reference 10 at end of chapter.
[17] Reference 10 at end of chapter.
[18] Reference 4 at end of chapter.
[19] Reference 11 at end of chapter.

known origin. The M lines are assumed to originate as follows: $M\alpha = M\,1 - N\,1$; $M\beta = M\,2 - N\,2$; $M\gamma = M\,3 - N\,3$. On the right side of Figure 38 are shown the series limits of the emission lines which indicate the initial states involved. The plotted differences give the final state for each emission line which also corresponds to an absorption limit. All M lines are plotted on one row and the M limits used are those computed from the L series lines. The upper row gives the mean positions of five M and seven N levels. The intervals $N\,1$, $N\,2$ and $N\,3$,

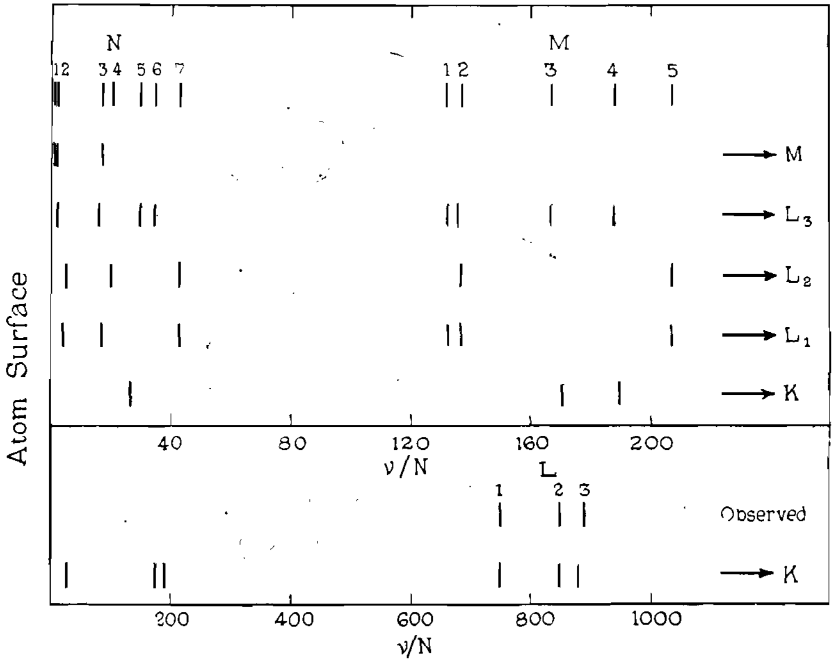


FIG. 38. Energy levels in the tungsten atom computed by the combination principle.

$N\,4$ for tungsten are smaller than the experimental error, but for uranium and thorium they are of measurable magnitude.

In Table XLI is given the origin of each line in accordance with Figure 38. The O limits are all unresolvable and close to the origin, so they have not been included in the diagram. All but two very faint lines are accounted for. It is seen that the series relationships furnish a logical system of nomenclature for x-ray lines analogous to the notation used for arc and spark spectra.

TABLE XLI

X-RAY SPECTRA OF TUNGSTEN

Notation	Observed ν/N	Series Notation	Computed Limit ν/N	Notation
K 1	5118.0			
$K\alpha$ 3	4239	K 1 − L 3	879	L 3
$K\alpha$ 2	4270.3	K 1 − L 2	848	L 2
$K\alpha$ 1	4368.7	K 1 − L 1	749	L 1
$K\beta$	4947.4	K 1 − M 3	171	M 3
$K\beta'$	4928	K 1 − M 4	190	M 4
$K\gamma$	5050.9	K 1 − N 5	27	N 5
L 1	750.88			
L 2	849.42			
L 3	889.9			
Ll	544.02*	L 1 − M 5	206.9	M 5
$L\alpha$ 2	613.85*	L 1 − M 2	137.0	M 2
$L\alpha$ 1	618.45*	L 1 − M 1	132.4	M 1
$L\eta$	642.78*	L 2 − M 5	207.0	M 5
$L\beta$ 4	701.66*	L 3 − M 4	188.2	M 4
$L\beta$ 6	708.00*	L 1 − N 7	42.9	N 7
$L\beta$ 1	712.39*	L 2 − M 2	137.4	M 2
$L\beta$ 3	723.23*	L 3 − M 3	166.7	M 3
$L\beta$ 2	733.76*	L 1 − N 4	17.1	N 4
$L\beta$ 8	736.4			
$L\beta$ 7	746.6*	L 1 − N 2	4.3	N 2
$L\beta$ 5	751.1*	L 1 − O	0	O
——	752.0			
——	753.3	L 3 − M 2	136.6	M 2
——	757.1	L 3 − M 1	132.8	M 1
$L\gamma$ 5	807.03	L 2 − N 7	42.7	N 7
$L\gamma$ 1	831.81*	L 2 − N 4	17.9	N 4
——	844.2	L 2 − N 2	5.5	N 2
$L\gamma$ 6	850.5	L 2 − O	0	O
$L\gamma$ 2	854.98	L 3 − N 6	34.9	N 6
$L\gamma$ 3	859.97	L 3 − N 5	30.0	N 5
——	873.5	L 3 − N 3	16.4	N 3
$L\gamma$ 4	887.77*	L 3 − N 1	2.1	N 1
$M\alpha$	130.56	M 1 − N 1	2.0	N 1
$M\beta$	134.99	M 2 − N 2	2.0	N 2
$M\gamma$	149.62	M 3 − N 3	17.1	N 3

* Denotes lines of experimentally determined series.

Figure 39 shows the M and N levels of uranium computed from the L and M series. In this case the five M levels have been observed spectroscopically so that the N limits computed from M lines are much more accurate than for tungsten. Other heavy elements give similar results and for atoms as light as caesium, $Z = 55$, several M and N levels may be located from data on the L series. L limits may be computed from K series lines down to magnesium, $Z = 12$. K spectra for elements lighter than titanium, $Z = 22$, become complicated by additional lines $K\alpha'$, $K\alpha_3$, $K\alpha_4$, $K\alpha_5$, $K\alpha_6$, and L limits computed from these lines are all softer than L 1, 2. Figure 35 shows lines drawn through

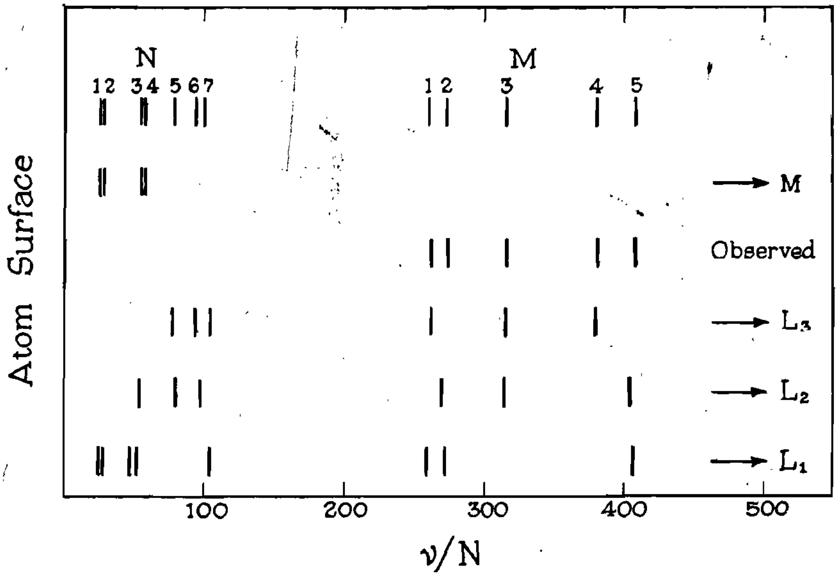


FIG. 39. Energy levels in the uranium atom computed from L and M spectra.

the mean points computed from the close doublets α_3, α_4 and α_5, α_6. It is seen that the computed points agree with the observed critical potentials, though only in one case, phosphorus, were the three potentials, corresponding to the three lines drawn, clearly separated.

Several theories have been proposed to explain these α lines all of which assume that the simple combination law cannot be applied; *i.e.* that the limit K 1 does not determine the initial state. The observation of L limits agreeing with the computed frequencies,

$$L\ 5, 6 = K\ 1 - K\alpha_{5,6} \text{ etc.,}$$

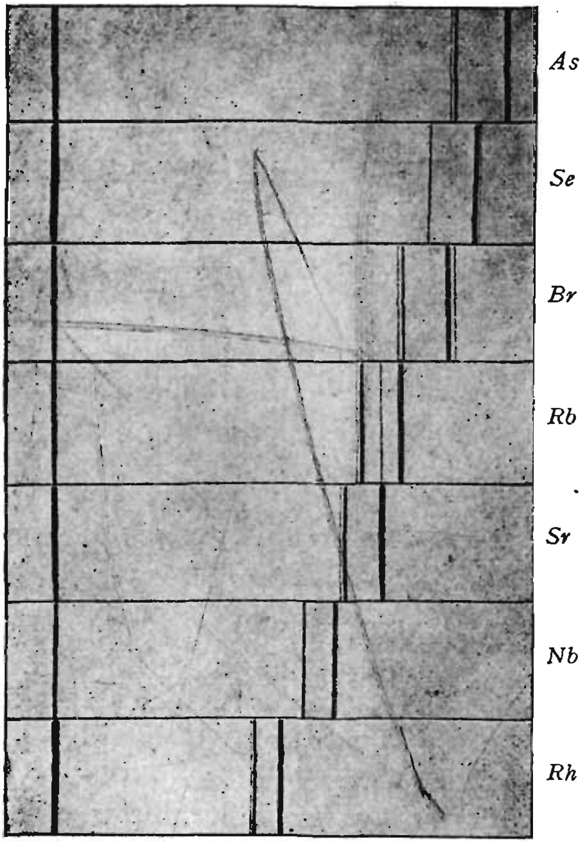


Fig. 36. K emission lines photographed by Siegbahn. (Reproduction is a negative.) The line at the left is a reference line. The strongest close doublet is $K\alpha_1$ and $K\alpha_2$.

cannot be explained by any such theory. For the same reason we cannot ascribe these L limits to resonance potentials. If the K limit is an ionization potential, $L5,6$ must be one also, provided the above relation has a physical basis.

4. Theoretical Significance of the System of Absorption Limits

It is evident from Figure 33 that the usual assumption that the atom structure is made up of single K, L, M, etc., levels is a very rough approximation. In a heavy element the five M limits and seven N limits each cover a range of frequency comparable to the interval separating the two groups. For uranium we must have, in addition to the sixteen limits shown, an undetermined number of O and P levels.

Disregarding for the instant the complexity of the limits, we see that the magnitude of the frequencies involved indicates the total quantum number n, which must be assigned to each group of levels K, L, M, etc. Thus the energy of a K level is a little less than that of a single electron in an $n = 1$ orbit around a nucleus of charge Ze. An electron in an outer level has energy comparable to an electron in a higher quantum orbit revolving around a charge $(Z - z)e$, (z = electron deficiency) so that to a first approximation the equation of a limiting frequency is

$$\nu/N = \frac{(Z - z)^2}{n^2}. \tag{135}$$

While this equation is far from accurate, yet it indicates that n has the values 1 for K, 2 for L, 3 for M, and 4 for N.

There are some striking regularities in the complicated groups of absorbtion limits.[20] They may be classified in two ways: (1) Pairs $L\,1\ L\,2$, $M\,3\ M\,4$, $M\,1\ M\,2$, $N\,5\ N\,6$, $N\,3\ N\,4$, and $N\,1\ N\,2$, which are converging lines on the Moseley diagram. The wave-length difference for each pair is constant for different elements. (2) The pairs $L\,2\ L\,3$, $M\,4\ M\,5$, $M\,2\ M\,3$, $N\,6\ N\,7$, $N\,4\ N\,5$, $N\,2\ N\,3$ give parallel curves on Figure 33. The law of their separation is then $\sqrt{\nu_1} - \sqrt{\nu_2}$ = constant.

It was shown in Chapter I that the separation $L\,1,2$ could be explained by the difference in relativity correction for two orbits, one of radial quantum $n_r = 0$ and azimuth quantum $n_a = 2$, the other $n_r = 1$ and $n_a = 1$. Sommerfeld finds that all doublets of the first type, $\Delta\lambda$ = constant, can be explained in the same manner.

[20] Reference 11 at end of chapter.

The equation for this doublet separation, Equation (62) Chapter I, can be written in the form

$$\Delta\nu/N = \gamma\,(Z - z)^4[1 + a\,(Z - z)^2 + b\,(Z - z)^4] \qquad (136)$$

where γ, a and b are constants involving the values of n_a and n_r used, and z is the electron deficiency in the orbit concerned. Values of n_a and n_r are chosen according to the scheme of Table XLII.

TABLE XLII

QUANTUM NUMBERS OF X-RAY LIMITS

Limit	K	L 1	L 2	L 3	M 1	M 2	M 3	M 4	M 5	N 1	N 2	N 3	N 4	N 5	N 6	N 7
n_a......	1	2	1	1	3	2	2	1	1	4	3	3	2	2	1	1
n_r......	0	0	1	1	0	1	1	2	2	0	1	1	2	2	3	3
$n_a + n_r$.	1	2	2	2	3	3	3	3	3	4	4	4	4	4	4	4

That the law $\Delta\lambda$ = constant is consistent with Equation (136) is easily seen. To an approximation, from Equation (135), it follows that for a given line of a given series in all elements,

$$\nu = k\,(Z - z)^2 \qquad \nu^2 = k^2\,(Z - z)^4.$$

By Equation (136), $\Delta\nu = k'\,(Z - z)^4$.

Since $\Delta\lambda = \Delta\nu/\nu^2$ we have $\Delta\lambda = k'/k^2$ = constant.

A further test of Equation (136) is best made by solving for z, using the values of n_a and n_r given in Table XLII. Sommerfeld has carried this computation throughout the range of experimental data and finds the value of z constant for corresponding doublets of different elements. The following mean values are obtained for the different doublets.

Doublet..........	L 1, 2	M 3, 4	M 1, 2	N 5, 6	N 3, 4	N 1, 2
z...............	3.50	8.25	13.16	16.3	25.7	33.9

The quantity z is a measure of the resultant repulsive force of electrons in the inner atom structure on an electron at the given level. To a first approximation it is numerically equal to the number of electrons inside the orbit considered. The value of z should then increase progressively from the K ring outward, being always greater for levels of smaller

energy. The above results fulfill this condition, viz. z (L 1, 2) < z (M 3, 4) < z (M 1, 2) < z (N 5, 6) < z (N 3, 4) < z (N 1, 2). The values are also of the expected magnitude. Thus there are 10 electrons within the M group for which $z = 8$ to 13. That this deficiency remains the same for different elements is likewise in agreement with our conception of the inner structure of atoms.

The second class of doublets (inaptly termed irregular doublets) for which $\sqrt{\nu_1} - \sqrt{\nu_2}$ = constant, are more simply explained. We obtain directly from Equation (135):

$$\left.\begin{aligned} \nu_1/N &= \frac{(Z - z'_1)^2}{n^2} \\ \nu_2/N &= \frac{(Z - z'_2)^2}{n^2} \end{aligned}\right\} . \qquad (137)$$

Accordingly
$$\sqrt{\nu_1/N} - \sqrt{\nu_2/N} = \frac{z'_2 - z'_1}{n}. \qquad (138)$$

That is, the second type of doublet separation can be ascribed to electrons in levels of the same quantum number ($n = n_a + n_r$) but differing in electron deficiency. (z' and z distinguish deficiencies computed from the two types of doublets.) Equation (137) is only an approximation so that z'_1 and z'_2 may differ considerably from the z's computed from relativity doublets. However the difference $z'_2 - z'_1 = \Delta z'_{1,2}$ should be the actual difference in electron deficiency if as we have assumed this is the sole cause of the frequency difference. All available data on these doublets give the following mean values.

	L 2, 3	M 2, 3	N 6, 7	N 4, 5	N 2, 3
$\Delta z'$.	1.21	3.39	2.3	4.7	9
Δz.		4.91		9.4	8.2

The lower row gives values of Δz computed from differences in z given by relativity doublets (z of M 1, 2 − z of M 3, 4 = Δz of M 2, 3, etc.). The agreement is not very close, but there is great uncertainty in some of the data as well as in the approximations. That the two differences are of the same sign and magnitude is a fair justification of the theory.

We conclude that the doublets of the first type; L 1 and L 2, M 1 and M 2, etc.; all originate from two orbits at the same mean distance from the nucleus but differing in ellipticity; while apparently the pairs of the

second type; *L* 2 and *L* 3, *M* 2 and *M* 3 etc.; are orbits of the same shape but at different distances from the nucleus.[21] Thus the *L* 3 orbit is inside of *L* 2 so that the electron deficiency for the latter orbit is increased by the effect of electrons in *L* 3. There are then two *L* levels, three *M* levels and four *N* levels; and at some of these levels are two types of orbit differing in ellipticity and hence in energy because of the relativity effect. This latter separation becomes negligibly small for the limits of low frequency. The *L* limits softer than *L* 1 observed only for light elements, do not fall within the above scheme. These lines on Figure 35 are evidently parallel and hence form doublets of the second type.

Two quantum numbers n_a and n_r suffice to explain the doublet separation and, roughly at least, the absolute values of the frequencies in x-ray spectra. If we attempt to find a selection principle in the emission spectrum another quantum number must be used. Wentzel[22] has developed a system involving a third "grund quantum *m*"[23] which explains the observed intensity relations and requires no change in the other quantum numbers. As with arc spectra, transitions violating the selection principle are improbable but not impossible. For details of this principle of selection the reader is referred to the original papers.

The laws of doublet separation furnish the criteria for extrapolating the curves of Figure 33 beyond the range of our data. Thus *L* 3 on the Moseley scale is parallel to *L* 2. The graphs of the relativity doublets converge as the atomic number decreases and the five *M* limits for light elements approach three parallel lines, *M* 1, 2, *M* 3, 4, and *M* 5. As a further guide for extrapolation we assume in analogy to the *L* series that *M* 1, 2 begins with the ionization potential of argon at 15.1 volts.

[21] But see in this relation Appendix II.

[22] Reference 10 at end of chapter.

[23] This is analogous to the "inner quantum" proposed to explain the selection principle involved in doublets and triplets of arc spectra. It is found that, with the exception of certain very faint lines, x-ray emission spectra, like arc and spark spectra, arise from transitions fulfilling the Rubinowicz selection principle; *viz.*, the change in n_a is ± 1 or 0. But the converse is not true. All transitions fulfilling this condition do not appear. For instance both $K\alpha_2 = K1 - L2$ and $K\alpha_3 = K1 - L3$ involve transitions in which $\Delta n_a = +1$. $K\alpha_2$ is always a strong line but $K\alpha_3$ is unobserved except in the tungsten spectrum as measured by Duane. Evidently there is in addition to the Rubinowicz limitation another limiting factor independent of the values of n_a and n_r. Wentzel expresses the law of selection as follows Assign to the x-ray orbits numbers *m* as given below:

	K	*L* 1	*L* 2	*L* 3	*M* 1	*M* 2	*M* 3	*M* 4	*M* 5	*N* 1	*N* 2	*N* 3	*N* 4	*N* 5	*N* 6	*N* 7
m..	1	2	2	1	3	3	2	2	1	4	4	3	3	2	2	1

Then observed emission lines (very faint lines excepted) arise in transitions for which $\Delta n_a = \pm 1$ or 0, $\Delta m = \pm 1$. At the present time we do not know the physical meaning of *m* or of changes in *m*.

It is seen in Figures 35 and 33 that critical potentials ascribed by Kurth to the N series, the potentials measured by the authors for potassium and nickel, and the molybdenum point found by Richardson and Bazzoni all fall close to the M 1 line. The three higher potentials measured by Kurth are close to M 5 and the point ascribed by the authors to tungsten falls on the N 1, 2 line.

Of the L limits observed by Kurth the points for aluminum and silicon fall exactly on L 3, while for heavier elements measured potentials are close to L 1. The fact that the authors did not observe L 3 is explained by the difficulty in distinguishing a faint critical potential which lies above a strong one. The failure of Kurth to observe the L 1, 2 limit indicates that there is a fundamental difference between soft x-radiation of solids and gases. We suggest the hypothesis that radiation from the outer x-ray orbits is at least partially suppressed in solids for the same reason that arc and spark spectra are entirely missing. In the second row of the periodic table the level L 1, 2 is close to the atom surface and L 3 considerably below it. Hence in the solid state only L 3 can freely emit radiation. Beyond the second row both L 1, 2 and L 3 are well within the surface and radiation from the former becomes strong. For the same reason, the emission spectra observed by Millikan for sodium, magnesium, and aluminum may belong to the L 3 series. The lines are not then $L\alpha$ but possibly $L\beta_3$ or $L\beta_4$. If the above hypothesis is admitted all serious discrepancies in critical potential measurements are removed and the observations agree within experimental error with the scheme of x-ray limits computed from high frequency spectra.

Conclusion

The system of x-ray absorption limits indicates the energy levels within the atom surface and must accordingly form the basis for any theory of atomic structure. The large number of the absorption limits suggests the difficulty of the problem. There have been several viewpoints as to the interpretation of these results. One is that in any single normal atom only one type of orbit appears in each K, L, M, etc., level.[24] This makes it possible to preserve the symmetry which it has been customary to ascribe to atom models, but unfortunately this assumption has other theoretical consequences, for example fine structure of K-lines, which are impossible to reconcile with experimental data.

We are apparently forced to the conclusion that all the shapes of

[24] Reference 11 at end of chapter.

orbits indicated by the theory of relativity-doublets appear in every atom. This is the viewpoint taken by Bohr[25] in his recently published theory of atomic structure (see Appendix II). If we refer to Figure 1 which gives the possible shapes of orbits up to quantum number 4 it will be evident that the simultaneous existence of all types of orbits in a heavy atom results in a very complicated structure. In addition to this complexity due to different shapes of orbits we have in the second type of doublets evidence of a difference in size among orbits of the same shape. Bohr, however, suggests that this frequency difference may be due to the existence of two possible configurations in the excited atom following the ejection of an electron from one normal orbit. In view of the apparent success of the explanation, on the basis of the existence of two normal orbits, we must, at least for the present, give it preference and conclude that absorption limits all correspond to energy levels in the normal atom.

The test of these theories will rest largely on more extensive and accurate data on absorption limits. As we have shown in this chapter, the problem can be approached both by direct measurements and by the computation of limits from emission spectra. The rapid progress of the past year in both directions encourages the belief that a fairly complete survey of the field will be available in the near future. As to the theoretical computation of energy levels, the apparent success of previous attempts may be misleading. The simple symmetrical electron configurations which have been assumed in such calculations bear little resemblance to the complicated structure indicated by experiment. The numerical agreement between computation and experiment over a limited range of x-ray spectra (all published results are limited to the K series) may be accidental. A complete solution of the problem is inconceivable at the present time, but a reconsideration of the assumptions necessary for an approximate solution is imperative.

REFERENCES

1. Critical potentials in the x-ray region.
Summary: Webster, Bul. Natl. Res. Council, 1, p. 432 (1920).
L series of tungsten and platinum: Hoyt, Proc. Nat. Acad. Sci., 6, p. 639 (1920).
M series: Ross, Phys. Rev., 18, p. 336 (1921).

2. Soft x-ray limits from critical potential measurements.
Mohler and Foote, Bur. of Standards Sci. Paper No. 425.
Kurth, Phys. Rev., 18, p. 461 (1921).
Richardson and Bazzoni, Phil. Mag. 42, p. 1015 (1921).
Hughes, Phil. Mag., 43, p. 145 (1922).

3. Corpuscular Spectra.
Rutherford, Rawlinson and Robinson, Phil. Mag., 28, pp. 277, 281 (1914).
M. de Broglie, Compt. rend., 172, pp. 274, 527, and 806; Compt. rend., 173, p. 527 (1921).

[25] Reference 12 at end of chapter.

4. Absorption spectra.
Summary: Duane, Bul. Natl. Res. Council, 1, p. 384 (1920).
de Broglie, J. phys., p. 161 (1916).
K series: Fricke, Phys. Rev., 16, p. 202 (1920).
L series: Hertz, Z. Physik, 3, p. 19 (1920).
M series: Stenstrom, Dissertation, Lund (1919).
Coster, Z. Physik, 5, p. 139 (1921).
5. Theory of structure of x-ray limits.
Kossel, Z. Physik, 5, p. 139 (1920).
6. Dependence of spectra on chemical composition.
Chlorine: Lindh, Z. Physik, 6, p. 303 (1921).
Phosphorus: Bergengren, Z. Physik, 3, p. 247 (1920).
7. Absorption coefficients for x-rays of long wave-length.
Holweck, Ann. phys., p. 1 (1922).
8. Data on emission spectra.
Siegbahn, Jahrbuch Rad. u. Elek., 13, p. 296 (1916).
Duane, *loc. cit.*, 4.
Stenstrom, *loc. cit.*, 7.
Hjalmar, Z. Physik, 7, p. 341 (1921).
Coster, Z. Physik, 4, p. 178 (1921).
9. Extension of the range of the diffraction grating.
Millikan, Proc. Nat. Acad. Sci., 7, p. 289 (1921).
10. Combinations in x-ray spectra.
Kossel, Verh. Deut. Phys. Ges., 16, pp. 899 and 953 (1914).
Duane, *loc. cit.*, 4.
Smekal, Z. Physik, 4, p. 26; 5, pp. 91 and 121 (1921).
Dauvillier, Compt. rend., 172, pp. 915 and 1350 (1921).
Coster, Z. Physik, 6, p. 185 (1921).
Wentzel, Z. Physik, 6, p. 84 (1921).
11. On regular and irregular doublets.
Sommerfeld, "Atombau und Spektrallinien," 3d Edition, p. 605.
Hertz, Z. Physik, 3, p. 19 (1920).
12. On the structure of atoms.
Bohr, Z. Physik, 9, p. 1 (1922).

Published since this Chapter was Written

On the Spectra of X-Rays and the (Bohr) Theory of Atomic **Structure.** **D. Coster,** Phil. Mag., 43, pp. 1070–1107 (1922).

The *N* Series Emission Spectrum of Uranium, Thorium and **Bismuth.** **V. Dolejsek,** Z. Physik, 10, pp. 129–136 (1922).

Chapter X

Photo-electric Effect in Vapors

It is well known that if a solid or liquid metal is illuminated with light of sufficiently high wave number ν, photo-electrons are emitted.[1] Below a minimum value of ν no emission takes place, but as ν is increased, the emitted electrons leave the surface with increasing initial velocity. The metals in the solid and liquid state are capable of absorbing the entire energy of the quantum of incident radiation. This energy is conserved and is represented by the kinetic energy of the emitted electron plus the work required to bring the electron through the surface of the metal.

By analogy we should expect a corresponding photo-electric effect for atoms in the vapor state. If the vapor is illuminated with light of the wave number corresponding to the highest convergence frequency in its arc spectrum, 1 s for the alkalis and 1 S for the metals of Group II, a quantum of this energy value should be sufficient to eject the valence electron from the atom with zero velocity. If the wave number exceeds this minimum value we might expect that the valence electron could be ejected with a velocity or kinetic energy $\frac{1}{2}mv^2 = hc\nu - hc\cdot(1\ S)$. It is conceivable on the other hand that the atom would respond to only the single wave number 1 S, the higher frequencies producing no effect upon the valence electron. We shall see however that there is good evidence against this latter hypothesis.

So far the ordinary methods of measuring the photo-electric effect by observing the photo-electric current between two plates immersed in the vapor which is illuminated by the ultra-violet source of light have yielded very little of a definite nature. The amount of photo-electric ionization has not been sufficient to have enabled any of the many investigators in this field to differentiate it clearly from spurious effects. In fact the very existence of a photo-electric effect should be responsible

[1] Hughes, "Photo-Electricity" Cambridge Univ. Press (1914). Supplemented by Bull. Nat. Res. Coun., 2, pp. 83–169 (1921).

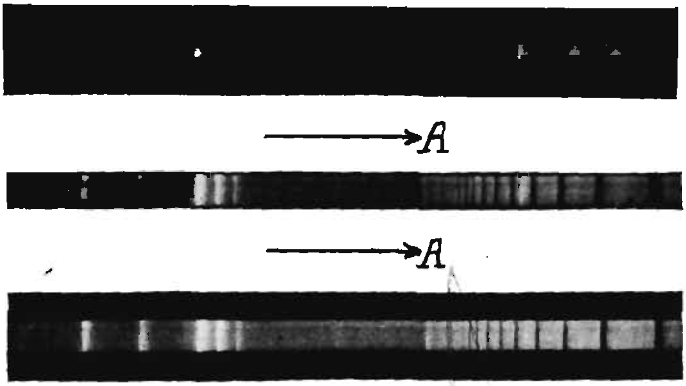


Fig. 40. Absorption of sodium vapor showing the presence of continuous absorption beginning at the convergence of the principal series and extending toward the shorter wave-lengths. Bright lines are due to the source of radiation.

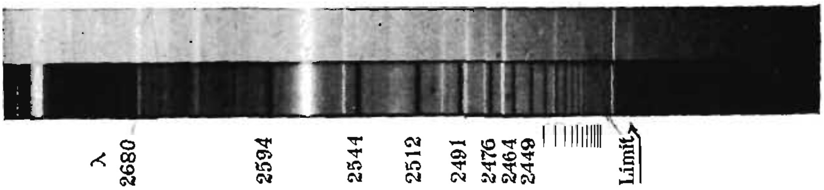


Fig. 41. The lower spectrogram shows the continuous absorption of sodium vapor beginning at the limit of the principal series and extending toward the shorter wave-lengths. The upper spectrogram shows the source of radiation alone.

for a spurious current consisting of electrons liberated from the electrodes by the diffused radiation from the vapor which must be an immediate consequence of photo-electric ionization. The chief difficulties encountered, however, have been in the shielding of the electrodes from direct and scattered radiation of the illuminating source, and the scattering by impurities, dust particles, condensed groups of atoms, or ions, etc.

A probable exception to the above statement is suggested by the recent note of Williams and Kunz[2] who found that caesium vapor was ionized by light of wave-length 2530A and that wave-lengths longer than λ 3130 were quite ineffective. Special care was taken to ensure the absence of surface effects. The value of 1 *s* for caesium is λ 3184.

The spectroscopic consequences of a photo-electric effect in vapors are most interesting. If any considerable effect existed, and if it required for its production radiation precisely corresponding to the convergence wave number of the principal series, we should expect to find a strong narrow absorption line at this point in the absorption spectrum of the normal vapor. No such phenomenon has been observed.

On the other hand if the photo-electric ejection of the valence electron may be produced by the absorption of radiation of any wave number greater than that corresponding to the highest convergence limit we might expect to find a well-defined broad band in the absorption spectrum terminating sharply on the long wave-length side at the convergence of the series. In fact this method would immediately suggest itself for the determination of series limits for elements for which the relations are unknown. This precise phenomenon has not been observed. We shall see that absorption is present but it is not in general very sharply defined.

If the ordinary photo-electric action is possible, illumination of the vapor with light of wave number equal to or greater than that of the highest convergence frequency should produce ionization. The ionization should be followed by recombination so that with such monochromatic stimulation all lines of the arc spectrum should be excited. The authors have tried this experiment with caesium vapor obtaining negative results. However, from the evidence presented below there is little question but that the emission should be produced. It is possible that the effect is present, but of insufficient intensity to be readily detected. The experiment is a crucial one and worthy of extensive investigation.

Complete ionization, or certainly nearly complete, may be produced in successive stages as shown by Fuchtbauer's[3] experiments

[2] Phys. Rev., 15, p. 550 (1920).
[3] Physik. Z., 21, pp. 635–8 (1920).

with mercury vapor. As discussed in detail in Chapters IV and VI, the mercury vapor illuminated by light from the mercury arc was found to *emit* the arc spectrum. Wood observed absorption of the 57th term in the principal series of sodium. The valence electron is accordingly ejected to the 58 p orbit and the atom is thus able to emit most of the arc lines. If the electron can be ejected to the 58 p orbit there is no question but that it can be completely ejected by absorption of radiation of slightly higher frequency, for the difference between the 58 p orbit and complete ionization is an extremely small quantity.

We have shown in Chapter IX that a limit in x-ray series is sharply defined by the edge of an absorption band. For example, dense absorption begins abruptly at the K limit and gradually fades away toward the higher frequencies. The reason that the band is well defined is because the other x-ray orbits are occupied. The electron in the K-orbit can not absorb a lower frequency sufficient to displace it to an L-orbit, for example, since the L-orbits are saturated and there is no vacant place which the ejected electron may occupy. The displacement must be to a virtual orbit which is unoccupied in the normal atom. In the case of x-rays these virtual orbits are so far out that displacement to any of them amounts to complete ejection as far as the energy or the spectral frequencies are concerned.

The case is totally different with the spectroscopic phenomena produced by the valence electron. Here *all* orbits outside the normal orbit occupied by the electron are virtual or unfilled. The electron may be displaced to any of an infinite number of virtual orbits by absorption of radiation. The main reason the lines of the principal series of sodium were not detected by Wood beyond $m = 58$ was because of insufficient resolution. The absorption is present but the 58 to ∞ terms are all so close together that they appear as a continuous band terminating at the convergence of the series. Now if the atoms could not absorb radiation of higher wave number than this, that is if there were no photo-electric effect, the absorption spectrum should terminate sharply at the convergence frequency. We would have a dark band from $m = 58$ to $m = \infty$ and the clear bright background of the continuous source at the higher frequencies. The phenomenon usually observed however is an apparently continuous absorption extending from, say $m = 58$ to wave-lengths much shorter than that corresponding to 1 s. That is, the apparent band spectrum due to the close line absorption joins on to the true band spectrum, at wave numbers greater than 1 s, and there is no abrupt change in the spectrum at 1 s. The band

spectrum at wave numbers greater than 1 *s* indicates the existence of the photo-electric effect in vapors.

Under certain experimental conditions it is possible to accentuate the amount of continuous absorption over that of the line absorption so that a slight discontinuity is observable at 1 *s*. Apparently one condition for this result is high vapor density. Figure 40 shows three absorption spectrograms for sodium vapor made from Professor Wood's original negatives. The higher terms of the principal series show as absorption lines on the right half of the figure. Unfortunately, the bright lines from the cadmium spark used as the continuous source detract somewhat from the appearance of the prints. However, one sees that, because of insufficient dispersion and resolution, the lines crowd together near the convergence forming what appears to be band absorption. At the point A which marks the head of the series a genuine, continuous absorption spectrum is present which extends to the left for a considerable distance into the ultra-violet. The point to which attention is specially directed is the fact that the absorption is considerably more pronounced over the spectral region indicated by the arrow than at the head of the series just to the right of the arrow. The source, however, if photographed alone, is of uniform brightness in this region. This illustration clearly demonstrates the presence of the continuous absorption beginning at the head of the series and extending toward the higher frequencies, a fact pointed out by Wood[4] in 1909. In his paper he states "One point of great interest noted with very dense sodium vapor is the general absorption which begins exactly at the head of the principal series and extends from this point down to the end of the ultra-violet. The vapor is much more transparent to the light between the absorption lines than in the region below the head of the series. The head of the series actually shows much brighter on this account than the rest of the spectrum below it."

This is again brought out by Figure 41, a photograph made by Dr. George Harrison under similar conditions. Below the limit, the continuous absorption is much greater than anywhere between the principal series lines from $m = 9$ to the limit. The upper spectrogram shows the cadmium source alone, the intensity of which is fairly uniform.

We have found in Chapter VI that if the vapor pressure is high an appreciable fraction of the atoms may be excited, the valence electron being maintained in the 2 *p* orbit by absorption of the temporarily imprisoned resonance radiation. Hence for such atoms there should be

[4] Astrophys. J., 29, pp. 97–100 (1909).

a region of continuous absorption defined sharply on the red side at 2 p or for sodium at about $\lambda = 4080$. There is an indication of this at the extreme left of the illustration. The wave-length concerned, however, lies outside the portion of the spectrogram here reproduced. One would expect that if such a continuous absorption were present, lines of the subordinate series should be reversed. However, it is worthy of note that under the above described conditions some continuous absorption may be expected at 2 p and at higher wave numbers such as 2 s, 3 d, 3 p, etc. This absorption, of course, will be superposed on the structured band spectrum arising in the molecule Na_2 and in general is probably too faint to be detected. Furthermore the different bands beginning at 3 p, 3 d, 2 s, 2 p, etc. probably overlap and give the appearance of a continuous stretch of faint absorption.

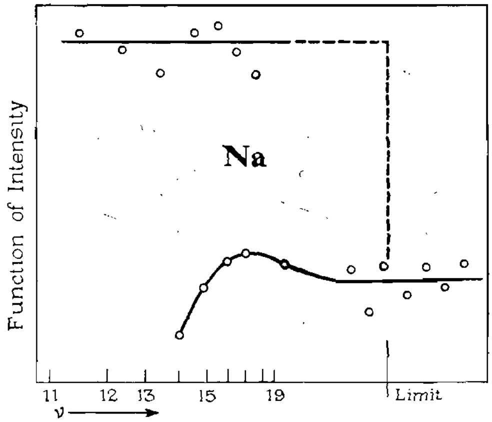


FIG. 42. Transmission of sodium vapor for radiation near the limit of the principal series.

Holtsmark[5] has made micro-photometric measurements on the transmission of a photographic negative throughout the region of the absorption spectra of sodium and potassium. The photographs were similar to those in Figures 40 and 41 except that lower vapor pressure was employed and there was no detectable transition from the line absorption to the band absorption. The negatives were of uniform density throughout this region. Figure 42 shows his results for sodium where the wave-length with increasing values toward the left is plotted against a *function of the intensity of the light transmitted by the column of vapor*.

[5] Physik. Z., 20, pp. 88–92 (1919).

The upper curve represents the observations on the portion of the spectrum lying between the lines, the ordinal numbers of which are indicated below. The lower curve from line 14 to the head of the series represents the photometric measurements made on the absorption lines themselves. The points to the right lying at higher frequencies than the head are due to the continuous absorption. One notes that the lower curve shows no abrupt change in passing the head of the series. The line absorption goes over into the band absorption without discontinuity. However, the comparison must be made with the upper curve. If it were not for the line absorption crowding together, making measurements between the lines impossible near the head, we would find the intensity curve following the course of the dotted line with a sharp break at the head. This is identically the type of curve char-

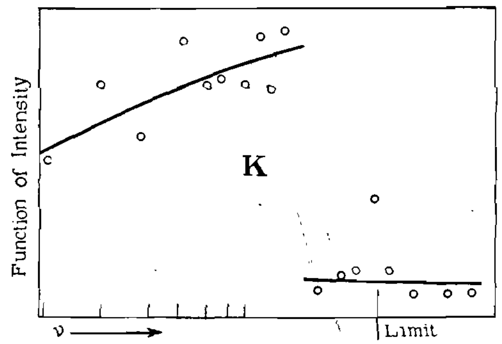


FIG. 43. Transmission of potassium vapor for radiation near the limit of the principal series.

acteristic of x-ray absorption limits. The only reason it is so difficult to detect in optical spectra is because the effect is in general obliterated or greatly reduced by the line absorption which is absent with x-rays.

Figure 43 shows similar results with potassium. The upper curve refers to the intensity between the lines and the lower curve to the intensity in the continuous band beginning with the head of the principal series. A sharp break appears at $\nu = 1\ s$, the limit.

We have mentioned that if continuous absorption is present at the head of the principal series we should also find it at the head of the subordinate series when a sufficient number of atoms are excited, having the valence electron in the 2 p ring. Thus with hydrogen, while the true photo-electric absorption of the normal vapor begins at the head of the Lyman series in the far ultra-violet, that of the excited gas should

begin at the head of the Balmer series and extend toward the shorter wave-lengths. In certain hydrogen stars as discussed in Chapter VII an appreciable fraction of the hydrogen atoms have the electron in the second orbit. Such stars should show a continuous band absorption limited on the less refrangible side at $\nu = \frac{1}{4} N_H$ or $\lambda = 3646$.

Huggins[6] observed that "a characteristic feature of white-star spectra consists in the rather sudden fall of intensity of the continuous spectrum at about the place of the end of the series of dark hydrogen lines. The spectrum, much enfeebled, continues to run on without any further sudden enfeeblement until it is stopped by the absorption of our atmosphere. This fall of intensity is most truly appreciated by comparing the brightness of the continuous spectrum in the narrow intervals between the last few hydrogen lines with the brightness of the continuous spectrum a little beyond the termination of the series of lines."

Hartmann[7] has made a systematic photometric study of several hydrogen stars and from numerous measurements concludes that there is a general absorption from the head of the Balmer series to about λ 3400.

Horton and Davies were led to conclude from their experiments on ionization potential, that helium, excited by 20.4 volt electronic impact, may be ionized by absorption of the 21.2 volt radiation of helium. If this observation be correct it indicates a photo-electric action analogous to that described for hydrogen.

In conclusion we find that while attempts to detect a photo-electric effect in vapors by electrical means have not yielded satisfactory results, the spectroscopic evidence for the existence of the effect is perfectly definite and that the phenomenon takes place precisely as predicted by the quantum theory of absorption.

[6] "An Atlas of Representative Spectra," p. 85.
[7] Physik. Z., 18, pp. 429–32 (1917).

Chapter XI

Determinations of h Involving Line Spectra

Birge[1] has summarized up to July, 1919, the determinations of Planck's constant h by seven independent methods and has concluded that the most probable value is $h = 6.554 \cdot 10^{-27}$ erg sec. This is the number employed for computation throughout this book.

Probably the most accurate means for the determination of h is by the application of the quantum relation to general x-radiation. Duane's[2] most recent value by this method gave $6.556 \cdot 10^{-27}$. We shall, however, confine our discussion to the methods, less precise at present, which involve the spectroscopic measurement of frequencies belonging to line series, for example, the limit of a principal spectral series, an x-ray limit, or a particular emission line.

There are three direct means for this: (1) by the x-ray method involving the correlation of the critical potential required to excite an x-ray series and the wave number or frequency of the limit of the series as determined by the absorption spectrum; (2) by use of the empirically determined value of the Rydberg constant N_∞ in Equation (7); (3) by measurements of ionization and resonance potentials and the corresponding spectral wave numbers, employing the quantum relation $hc^2\nu = eV \cdot 10^8$.

Characteristic x-rays

Table XLIII summarizes typical data on the determination of h by this method. We have seen in Chapters I and IX that as the kinetic energy of the impacting electron is increased by raising the accelerating voltage, a critical value is reached which is just sufficient to produce complete ejection of an electron from an x-ray ring. Because of this ejection, for example from the K-ring, a vacant space is created into which an L-electron falls with the resulting emission of $K\alpha$ etc. One, accordingly, observes the minimum potential, V, at which the K lines

[1] Phys. Rev., 14, pp. 361–8 (1919), see also Ladenburg, Jahrbuch Rad. u. Elek., 17, p. 93 (1920).

[2] Duane, Palmer and Chi-Sun-Yeh, J. Opt. Soc. Am., 5, pp. 376–87 (1921).

are excited. This is correlated with the absorption limit λ by the quar tum relation:

$$h = \frac{eV\lambda_{cm} \cdot 10^8}{c^2} = 5.309 \cdot 10^{-23}\ V\lambda_{cm}, \tag{139}$$

where $e = 4.774 \cdot 10^{-10}$ e.s.u. and $c = 2.9986 \cdot 10^{10}$ cm/sec., the wave length λ being expressed in cm.

There is little doubt but that the method is capable of far greate precision than is indicated by the values in Table XLIII. The techniqu has not been developed because of the more satisfactory method involv ing the general x-radiation. The recent value for aluminum by Holwec was obtained in a different manner as described on page 202.

TABLE XLIII

DETERMINATION OF h BY CHARACTERISTIC X-RAYS

Element	Limit	$\lambda \cdot 10^8$ cm Duane	Minimum voltage	$h \cdot 10^{27}$	Investigator
Mo......	K	.6184	19200	6.30	Wooten *
Rh......	K	.5330	23300	6.59	Webster **
Pd.......	K	.5075	24000	6.47	Wooten *
W.......	K	.1781	70–80000	6.7	Hull and Rice †
Pt.......	L_1	1.070	11450	6.50	Webster and Clark ††
	L_2	.932	13200	6.54	Webster and Clark
Al.......	K	7.947	1555	6.56	Holweck, cf. Table 4C

* Phys. Rev., 13, pp. 17–86 (1919).
** Phys. Rev., 7, pp. 599–613 (1916).
† Proc. Nat. Acad. Sci., 2, pp. 265–70 (1916).
†† Phys. Rev., 9, p. 571 (1917).

THE RYDBERG NUMBER

Equation (7), derived theoretically, in which N_∞ denotes the Ryd berg series constant for an element having a nucleus of infinite mass gives directly for h:

$$h = \sqrt[3]{\frac{2\,\pi^2 e^5}{c\,(e/m)\,N_\infty}}. \tag{140}$$

The relation between N_∞ and N for a nuclear mass M is expressed b Equation (8). From empirically determined values of N_H and N_H

obtained by a consideration of the lines of hydrogen and ionized helium respectively, Paschen[3] found that

$$N_{\infty} = 109737.11.$$

This value may be readily verified by use of Equations (8) and (10), the independent determinations with hydrogen and helium agreeing to the last significant figure given.

The value of e/m may be also derived from observations on the wave-lengths of the hydrogen and helium lines as shown by Equation (12). This optically determined quantity is $e/m = 5.343 \cdot 10^{17}$ e.s.u./g. Substituting these values in Equation (140) we find:

$$h = 6.53 \cdot 10^{-27} \text{ erg sec.},$$

where the controlling error should be in the magnitude of the elementary charge and in e/m.

Ionization and Resonance Potentials

If we use the values of the ionization and resonance potentials listed in Tables X, XI and XXIV and the corresponding wave numbers which are known with high precision from spectroscopic determinations, we may employ the quantum relation to obtain a value for h as follows:

$$h = \frac{Ve \cdot 10^8}{c^2 \nu} = \frac{10^{-22}}{1.8834} \frac{V}{\nu} \cdot \tag{141}$$

The authors, in 1920, summarized their own data, to that date, which included twenty independent points on various elements, each of course a mean of a large number of measurements.[4] Equal weight was given to each observation with the resulting mean $h = 6.55 \cdot 10^{-27}$. Since then more points have been obtained by ourselves and others. We have plotted in Figure 44 thirty-three values, listed in the tables referred to, for which the spectroscopic frequencies are known. Assigning equal weight to each determination the mean value, $h = 6.544 \pm 0.015$ probable error, is obtained.

There is no doubt but that this method properly carried out will yield results of a precision comparable to that obtained by the best of the other methods. Up to the present time the primary object has been to determine critical potentials for a large number of elements and little attention has been given to the conditions favorable for the measurement of h. For example, a metal like calcium which can be handled only with

[3] See Chapter I. Computed from Paschen's values on N_H and N_{He}, cf. Ann. Phys. 50, p. 935 (1916).

[4] Foote and Mohler, J. Opt. Soc. Am., 2–3, pp. 96–9 (1919).

difficulty, is of little service in this regard. By using the recently developed refinements in the measurement of critical potentials and by

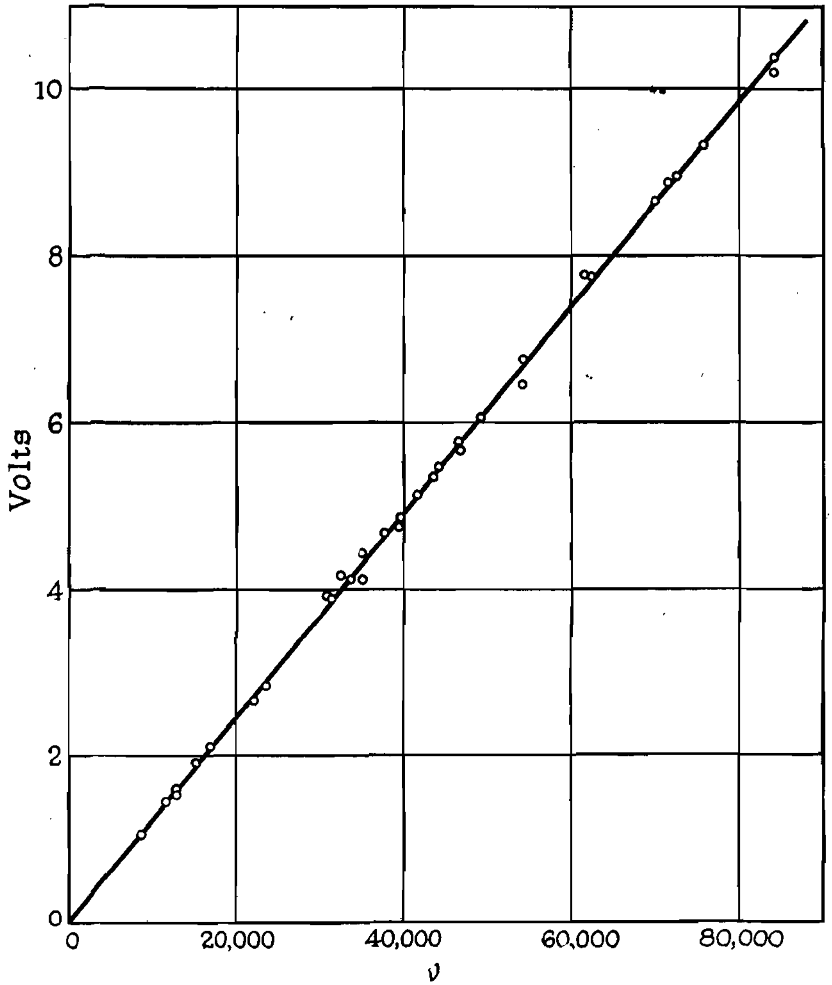


Fig. 44. Determination of h by ionization and resonance potentials.

employing a method of magnetic dispersion to produce a univelocity stream of electrons, high precision in h may be expected with an easily controlled vapor such as mercury.

Appendix I

Computational Data

TABLE XLIV

VALUES OF NUCLEAR DEFECT, s_n, (CF. Equation 44)

n	s_n	n	s_n
1	0	14	6.159
2	0.250	15	6.764
3	0.577	16	7.379
4	0.957	17	7.991
5	1.377	18	8.624
6	1.828	19	9.27
7	2.305	20	9.92
8	2.805	21	10.57
9	3.328	22	11.24
10	3.863	23	11.92
11	4.416	24	12.60
12	4.984	25	13.29
13	5.565	26	13.98

TABLE XLV

NUMERICAL MAGNITUDES

h	$6.554 \cdot 10^{-27}$	e	$4.774 \cdot 10^{-10}$	π	3.142	m_0	$8.93 \cdot 10^{-28}$
h^2	$4.295 \cdot 10^{-53}$	e^2	$2.279 \cdot 10^{-19}$	π^2	9.870	m_0^2	$7.97 \cdot 10^{-53}$
h^3	$2.815 \cdot 10^{-79}$	e^3	$1.088 \cdot 10^{-28}$	π^3	31.01	$N_\infty hc$	$2.157 \cdot 10^{-11}$
h^4	$1.845 \cdot 10^{-105}$	e^4	$5.194 \cdot 10^{-38}$	π^4	97.42	$\frac{h^2}{8\pi^2 m_0}$	$6.04 \cdot 10^{-28}$
h^5	$1.209 \cdot 10^{-131}$	e^5	$2.48 \cdot 10^{-47}$	$\sqrt{\pi}$	1.772	$\frac{e}{m_0}$	$5.34 \cdot 10^{17}$ e.s.u./g.
c	$2.9986 \cdot 10^{10}$	$\frac{2\pi e^2}{hc}$	$=\alpha = 7.29 \cdot 10^{-3}$	α^2	$5.31 \cdot 10^{-5}$	N_∞	109737·11

$$\text{Volts} = V = \frac{c^2 h}{e\lambda_A} = \frac{12345}{\lambda_A} \qquad (\lambda_A \text{ measured in Angstroms})$$

$$\text{Volts} = V = \frac{c^2 h\nu}{e} 10^{-8} = 1.2345\,\nu \cdot 10^{-4} \qquad (\nu = \text{wave number})$$

$$\nu = \frac{1}{\lambda_{cm}} = \frac{10^8}{\lambda_A} \qquad \text{(wave-lengths reduced to vacuo)}$$

$$\nu = 8100\,V \qquad \bar{\nu} = \text{frequency} = c\,\nu$$

Number molecules/gm mol $= 6.06 \cdot 10^{23}$

Number molecules/cm^3 at 760 mm and 0° C $= 2.705 \cdot 10^{19}$

Faraday constant $= 96500 \pm 10$ coulombs

One 20° cal. $= 4.183 \cdot 10^7$ ergs

(20° cal./gm mol) $\div$ 23070 = Volts/molecule

(Kg cal./gm mol) $\div$ 23.07 = Volts/molecule

Ergs $= 1.592 \cdot 10^{-12} \times$ volts

Ergs $= 1.965 \cdot 10^{-16}\,\nu$

$\nu = 5.088 \times \text{ergs} \cdot 10^{15}$

Gas constant $= R = 8.315 \cdot 10^7$ ergs/deg. C. (referred to mol of gas)

$= 1.985$ g cal./deg. C. (referred to mol of gas)

Kinetic energy of translation of av. molecule at 0° C $= 5.62 \cdot 10^{-14}$ ergs

Velocity of singly charged ion $= 1.389 \cdot 10^6 \sqrt{\frac{V}{M}}$ cm/sec. (V = volts, M = molecular weight)

Root mean square velocity $= C = 1.579 \cdot 10^4 \sqrt{T/M}$ cm/sec. (T = abs. temp., M = mol. wt.)

Mean free path of electron in gas $= 1/\pi r^2 n$ cm. (r = radius of gas molecule, n = number of molecules/cm^3)

Velocities of Electrons, Ions and Molecules

(Explanation of Figure 45)

The relation between the molecular weight, M, of an ideal gas, its absolute temperature T, and the root mean square velocity C of a molecule is given by

$$C = \sqrt{3\,RT/M} \quad = 1.579 \cdot 10^4 \sqrt{T/M} \text{ cm/sec.},$$

where R is the gas constant, $8.315 \cdot 10^7$ ergs/° C.

I. *To obtain C, knowing T and M*: Lay a straight-edge from M on scale (1) to T on scale (4). At the intersection with scale (2) read C in cm/sec. Example: The helium atom ($M = 4$) at a temperature of 20° C ($T = 293°$ K) has a root mean square velocity $1.38 \cdot 10^5$ cm/sec.

II. *To obtain the thermal velocity of an electron:* Lay a straight-edge from the electron point on scale (1) to T on scale (4). Read its intersection with scale (2) and multiply by 100 (since a mass 10^4 times too large has been used).

The relation between v, the velocity of a singly charged ion of mass m, and the voltage V producing that velocity, is:

$$\tfrac{1}{2}\, mv^2 = eV \cdot 10^8/c = eV/300,$$

also $e/m = f/M$, where $f = 96500$ coulombs $= 1$ faraday $= 9650c$ e.s.u. of charge.

$$\therefore v = 1.389 \cdot 10^6 \sqrt{V/M} \text{ cm/sec.}$$

III. *To obtain v for a simply charged ion, knowing V and M* (where V lies between 0.1 and 100 volts) lay a straight-edge from M on scale (1) to V on scale (6). At the intersection with scale (3) read velocity of ion in cm/sec.

IV. To obtain the velocity of an electron after acceleration by a voltage V lying between 0.1 and 100: Lay a straight-edge from the electron point on scale (1) to V on scale (6), read its intersection with scale (3) and multiply by 100 (since a mass 10^4 times too large has been used). Example: A 4.9 volt electron has a velocity, $100 \cdot 1.32 \cdot 10^6 = 1.32 \cdot 10^8$ cm/sec.

(If the voltage V is greater than 100, proceed as follows.)

V. To obtain v for an ion, knowing V and M: Proceed as in *III*, using 1/100 of the voltage on scale (6), and multiply the result by 10. Example: The velocity of a singly charged mercury atom ($M = 200$), after falling through 110 volts, is 10 times $1.03 \cdot 10^5 = 1.03 \cdot 10^6$ cm/sec.

VI. *To obtain v for an electron, knowing V and M.* Lay a straightedge from the electron point on scale (1), to 1/100 of the voltage on scale (6). Read the intersection with scale (3) and multiply by 1000. Example: A 110 volt electron has a velocity 1000 times $6.2 \cdot 10^5 = 6.2 \cdot 10^8$, change of mass with velocity being left out of account.

Scales (5) and (6) give directly the wave-length of the quantum emitted by an atom when it collides inelastically with a V volt electron.

The reader will be able to work out many other combinations. The principle of the chart is simple. It will be noted that all the scales have a similar logarithmic spacing. Scales (1), (2), (4) belong together, as do also scales (1), (3), (6), scale (1) doing double service to save space. We have, for example:

$$\log C = \log (1.579 \cdot 10^4) + \tfrac{1}{2} \log T - \tfrac{1}{2} \log M.$$

In using the chart as in I, we subtract graphically $\frac{1}{2} \log M$ from $\frac{1}{2} \log T$. The graphical addition of $\log (1.579 \cdot 10^4)$ has been cared for by shifting the origin of scale (2) with respect to the origins of (1) and (4). Similar remarks hold true for the relation between v, V, and M.

The chart cannot be applied directly to multiply charged ions, but it is easy to read the results for a singly charged ion and to multiply by the appropriate factor as found from the formulae given above.

The authors are indebted to Mr. W. H. Holden for suggesting the usefulness of such charts and to Mr. Arthur E. Ruark for preparing this particular arrangement. If the reader has occasion to do much rough computational work of this character, he will find that the few moments spent in studying the principle of this chart will be amply repaid.

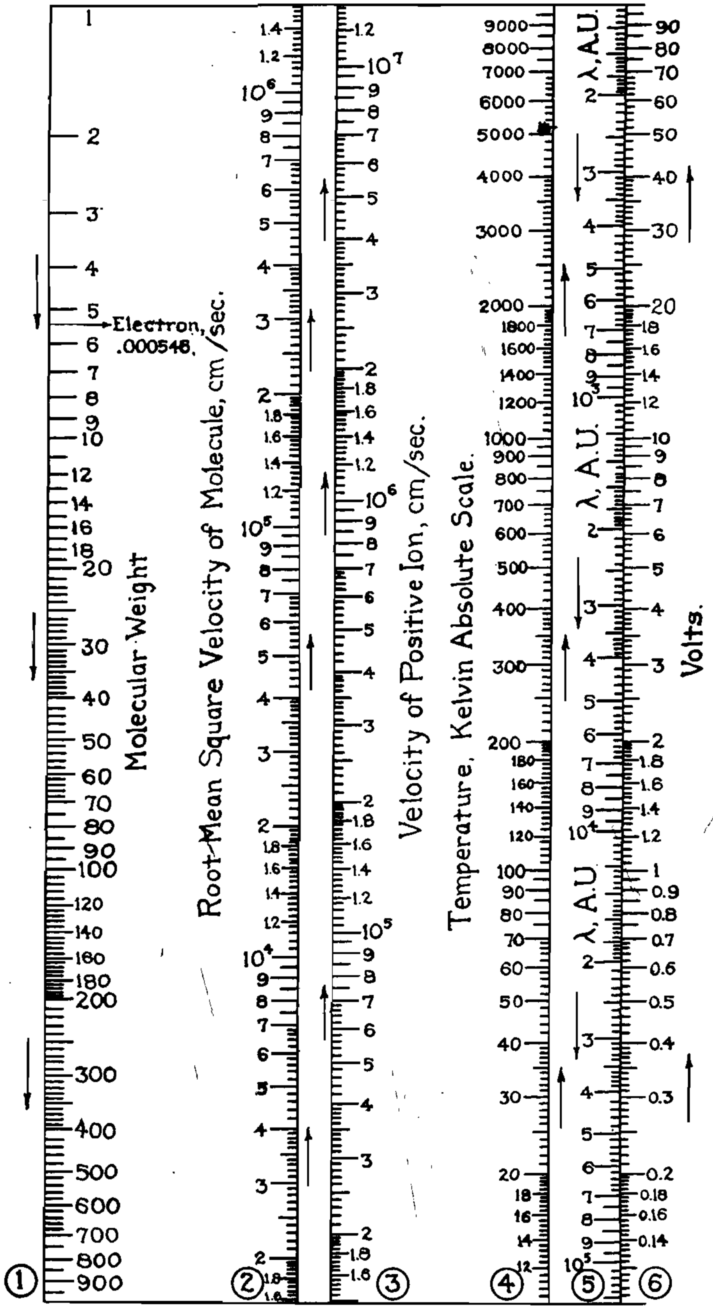


FIG. 45. Velocities of electrons, ions and molecules.

TABLE 46

PERIODIC CLASSIFICATION OF THE ELEMENTS

	I		II		III		IV		V		VI		VII		VIII & 0			
1	1 H 1.008																	2 He 4.00
2	3Li 6.94		4Be 9.1		5B 10.9		6C 12.005			7N 14.008		8O 16.00		9F 19.0				10Ne 20.2
3	11Na 23.00		12Mg 24.32		13Al 27.0		14Si 28.1			15P 31.04		16S 32.06		17Cl 35.46				18A 39.9
4	19K 39.10		20Ca 40.07		21Sc 45.1		22Ti 48.1		23V 51.0		24Cr 52.0		25Mn 54.93		26Fe 55.84	27Co 58.97	28Ni 58.68	
		29Cu 63.57		30Zn 65.37		31Ga 70.1		32Ge 72.5		33As 74.96		34Se 79.2		35Br 79.92				36Kr 82.92
5	37Rb 85.45		38Sr 87.63		39Yt 89.33		40Zr 90.6		41Cb 93.1		42Mo 96.0		43*		44Ru 101.7	45Rh 102.9	46Pd 106.7	
		47Ag 107.88		48Cd 112.40		49In 114.8		50Sn 118.7		51Sb 120.2		52Te 127.5		53I 126.92				54Xe 130.2
6	55Cs 132.81		56Ba 137.37		RARE EARTHS				73Ta 181.5		74W 184.0		75*		76Os 190.9	77Ir 193.1	78Pt 195.2	
		79Au 197.2		80Hg 200.6		81Tl 204.0		82Pb 207.20		83Bi 209.0		84Po (210.0)		85*				86Nt (222.4)
7	87*		88Ra 226.0		89Ac (226)		90Th 232.15		91PAc (230)		92U 238.2							

RARE EARTHS							
57La 139.0	58Ce 140.25	59Pr 140.9	60Nd 144.3	61*	62Sa 150.4	63Eu 152.0	64Gd 157.3
65Tb 159.2	66Dy 162.5	67Ho 163.5	68Er 167.7	69TmI 168.5	70Yb 173.5	71Lu 175.0	72TmII (178)

ATOMIC NUMBER AT LEFT OF EACH ELEMENT – ATOMIC WEIGHT BELOW

Appendix II

Bohr's Theory of Atomic Structure[1]

The system of electron configurations in non-hydrogen types of atom recently proposed by Bohr is a radical departure from the atomic models heretofore suggested. As yet *none of the mathematical steps* in the development of the theory have been published, and hence most of the following outline will appear purely empirical.

In reality, however, the new theory is an attempt to avoid arbitrary assumptions as to atomic structure. Bohr postulates that the normal electron configuration about a nucleus Ze must be such as would result by adding Z electrons, one at a time, to the structure, so that each electron occupies that orbit which is most stable with respect to the nucleus and previously bound electrons. This excludes the possibility of either a ring configuration or of groups of electrons in polyhedral symmetry. The ring structure appears to require the simultaneous binding of all the electrons in the symmetrical group. On the basis of the new theory each electron will occupy a separate orbit and will be to a large extent independent of other electrons in the same group.

We can investigate directly only the last stages of the atom building as shown in arc and spark spectra. A convenient approach to the problem of the earlier steps in the formation of a heavy atom is found in a study of successive elements in the periodic table. The stages are marked, by the periodic appearance of groups of electron orbits of increasing total quantum number, and by the subdivision of each group into orbits of different degrees of ellipticity.

Periods in atom structure correspond to intervals between rare gases in the periodic table. Table XLVIII shows the electron distribution in these gases and at certain intermediate stages. Table XLIX gives the transitions in structure between the stages shown in Table XLVIII. The following paragraphs are in explanation of the system outlined in the tables.

[1] Z. Physik, 9, p. 1 (1922).

To picture the different shapes of orbits it will be helpful to refer to Figure 1, Chapter I, which illustrates possible types of hydrogen orbits to quantum number 4. These are, at least to a first approximation, the types of orbit appearing in heavier atoms, the essential difference being that only one orbit is occupied in this figure while in general as many orbits are occupied as there are electrons in the atom.

First Period. — The theory of the hydrogen atom remains unchanged and its line spectra show us the separate steps in the binding of the first electron. The final state is a circular orbit of quantum number 1. The binding of the first electron in helium or any heavier element is similar except that the factor Z^2 enters into the energy equations.

TABLE XLVII

QUANTUM NUMBER NOTATION

Total Quantum n	Azimuthal Quantum n_a	Radial Quantum n_r	Bohr Notation n_{n_a}	Shape of Orbit
1	1	0	1_1	circle
2	2	0	2_2	circle
2	1	1	2_1	ellipse
3	3	0	3_3	circle
3	2	1	3_2	ellipse
3	1	2	3_1	ellipse

The introduction of the second electron marks the departure from former viewpoints. In the normal atom the two electrons are each in one quantum orbits (circles to a first approximation) the planes of which make with each other an angle of 120°. (See Chapter III, section on helium and Figure 11.) This configuration (I of Table XLVIII) remains unchanged for the first two electrons in all heavier elements.

It is assumed that for any further additions to the atom structure one quantum orbits are no longer possible. With groups of higher quantum number, we will have the appearance of sub-groups differing in orbital ellipticity. A notation is used by Bohr which is more convenient in this connection than specification of azimuth and radial quantum number; viz., total and azimuth numbers, as shown in Table XLVII.

TABLE XLVIII

STAGES IN THE BUILDING OF ATOMS DISTRIBUTION OF ELECTRONS IN SUB-GROUPS

Reference Number	Element	Quantum Numbers of Sub-groups														
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	6_1	6_2
I	He 2	2														
II	Ne 10	2	4	4												
III	A 18	2	4	4	4	4										
III′	Cu to Kr*	2	4	4	6	6	6									
IV	Kr 36	2	4	4	6	6	6	4	4							
IV′	Ag to Xe*	2	4	4	6	6	6	6	6	6						
V	Xe 54	2	4	4	6	6	6	6	6	6		4	4			
V′	Au to Nt*	2	4	4	6	6	6	8	8	8	8	6	6	6		
VI	Nt 86	2	4	4	6	6	6	8	8	8	8	6	6	6	4	4
		K 1	L 2 L 3	L 1	M 4 M 5	M 2 M 3	M 1	N 6 N 7	N 4 N 5	N 2 N 3	N 1	O			P	
		X-ray limits having above quantum numbers														

* These rows give only the sub-structure which remains unchanged in the interval indicated.

Second Period. — In normal lithium the third electron is in a two quantum elliptical orbit 2_1. The binding process is seen in the arc spectrum. In the three following elements the additional electrons likewise fall in 2_1 orbits. We must assume that these have a space configuration symmetrical with respect to each other and to the two orbits of the helium-like sub-structure.

Additional electrons in nitrogen, oxygen, fluorine and neon fall in 2_2 circular orbits. The neon structure (II, Table XLVIII) must be exceptionally stable and symmetrical and represents the configuration of the first ten electrons in all heavier elements.

Third Period. — In the following row of the periodic table 3_1 and 3_2 orbits are added to the neon sub-structure in an order similar to the building of the two quantum group in the second period. The binding of the eleventh and twelfth electrons gives the line spectra of sodium and magnesium. The period is closed with the stable argon structure III. However, the outer structures of argon and heavier rare gases are not completed groups, and, unlike the helium and neon structures, these configurations appear in the sub-structure of only a few elements.

Fourth Period. — Potassium and calcium have 4_1 orbits, giving them properties like sodium and magnesium, but with further increase in the nuclear charge a new type of transition appears. The 3_3 orbits become more stable than 4_1, so that successive electrons are added to the sub-structure III, in an order not yet determined, until the three quantum group is completed as in III′. This latter configuration does not occur alone in any element, but is the sub-structure of the elements copper to krypton. These have in addition to III′, 4_1 and 4_2 orbits similar to those of the superficial groups in the second and third periods.

Fifth Period. — This period is built in a manner analogous to that of the fourth. The 5_1 orbits give to rubidium and strontium the characteristic properties of the alkalis and alkali earths, respectively, and then ten electrons are added to the krypton sub-structure IV, producing the structure IV′. From silver to xenon the eight electrons of the 5_1 and 5_2 orbits are added to furnish the structure V of xenon.

Sixth Period. — Beyond caesium and barium there is a more extensive change in the sub-structure. First the four quantum group is completed by the addition of fourteen electrons (the rare earths) and then ten electrons are added to the five quantum group to complete the sub-structure V′. From gold to niton eight electrons in 6_1 and 6_2 orbits are added to form a characteristic rare gas structure VI.

Seventh Period. — After niton another long period is initiated.

TABLE XLIX

Transitions in Atom Structure Intermediate between Stages of Table XLVIII
Distribution of Outer Electrons

	H 1_1 1						
He I	Li 2_1 I $+1$	Be 2_1 I $+2$	B 2_1 I $+3$	C 2_1 I $+4$	N 2_1 2_2 I $+4+1$	O 2_1 2_2 I $+4+2$	F 2_1 2_2 I $+4+3$
Ne II	Na 3_1 II $+1$	Mg 3_1 II $+2$	Al 3_1 II $+3$	Si 3_1 II $+4$	P 3_1 3_2 II $+4+1$	S 3_1 3_2 II $+4+2$	Cl 3_1 3_2 II $+4+3$
A III	K 4_1 III $+1$	Ca 4_1 III $+2$	Si to Ni	eight elements Transition in sub-structure III–III′			
* III′	Cu 4_1 III′ $+1$	Zn 4_1 III′ $+2$	Ga 4_1 III′ $+3$	Ge 4_1 III′ $+4$	As 4_1 4_2 III′ $+4+1$	Se 4_1 4_2 III′ $+4+2$	Br 4_1 4_2 III′ $+4+3$
Kr IV	Rb 5_1 IV $+1$	Sr 5_1 IV $+2$	Yt to Pd	eight elements Transition in sub-structure IV–IV′			
* IV′	Ag 5_1 IV′ $+1$	Cd 5_1 IV′ $+2$	In 5_1 IV′ $+3$	Sn 5_1 IV′ $+4$	Sb 5_1 5_2 IV′ $+4+1$	Te 5_1 5_2 IV′ $+4+2$	I 5_1 5_2 IV′ $+4+3$
Xe V	Cs 6_1 V $+1$	Ba 6_1 V $+2$	La to Pt	twenty-two elements Transition in sub-structure V–V′			
* V′	Au 6_1 V′ $+1$	Hg 6_1 V′ $+2$	Tl 6_1 V′ $+3$	Pb 6_1 V′ $+4$	Bi 6_1 6_2 V′ $+4+1$		
Nt VI		Ra 7_1 VI $+2$	Ac to U	four elements Transition in sub-structure VI–VI′			

* These structures only appear as sub-structures in heavier elements.

For each element are given the quantum numbers of the last bound groups of electrons and the numbers of electrons in these roups. Thus for nitrogen the symbols have the following meaning.

Nitrogen contains outer orbits of quantum number 2_1 and 2_2. It consists of sub-structure I (Table XLVIII) and in addition four electrons in 2_1 orbits and one electron in a 2_2 orbit.

Radium contains two electrons in 7_1 orbits. Other transitions cannot be specified. The fact that no elements beyond uranium are known is explained, not by any property of the electron configuration, but by the instability of heavy nuclei, as evidenced by their radio-activity.

We will review briefly some of the properties of the new Bohr atoms which can be tested by experiment.

X-ray Spectra. — The evident interpretation of the origin of x-ray series on the basis of the above outlined atomic structure is that the K, L, M, etc., spectra originate in the groups of orbits of total quantum number 1, 2, 3, etc., respectively, and that each series starts with the rare gas in which the corresponding group of orbits first appears. This is in exact accord with the conclusions based on x-ray data as to total quantum number and origin of the different series (Chapter IX). Furthermore, the Sommerfeld theory of doublet separations shows that the orbits of each group have all the degrees of ellipticity permitted by the quantum theory. Thus we have experimental evidence for both the existence and order of appearance of the types of orbit postulated by Bohr. Table XLVIII gives in the lower rows the x-ray limits corresponding to the different sub-groups.

Superficial Atomic Properties. — The configurations of the last bound electrons, shown in Table XLIX, must determine nearly all the chemical and physical properties of the elements apart from x-ray phenomena. It is seen that the first electrons appearing in each group have orbits of azimuth quantum one. It is impossible to foresee what the exact form of such an orbit will be, for it is in a field of force which departs widely from a Coulomb field. Assuming though that Figure 1 gives the approximate form and relative size of the orbit, we conclude that electrons in these orbits will all penetrate the entire atom structure and at perihelion will be close to the nucleus of charge Ze. This is in marked contrast to other theories, all of which have assumed that the last bound electrons move in a field of approximately unit charge. At aphelion the electrons will lie far outside the structure of previously bound groups. The tendency of an atom to lose an electron (electropositiveness) will depend on the extension of the outer part of this orbit. It will be greatest for the alkali metals and will decrease progressively from left to right in each row of the periodic table. The number of electrons which may be lost (positive valence) correspondingly increases.

The second sub-group formed has an azimuth number 2. These orbits will not extend beyond previously bound groups and the electrons are not readily lost. On the contrary, elements preceding the rare

gases, the electro-negative elements, tend to take up electrons to form the stable rare gas configuration. The electro-positive or -negative properties do not necessarily imply small or large ionization potentials. The ionization potential is a measure of the total energy of an orbit; the electro-positive or -negative property depends on the extension or degree of ellipticity of the orbit as well as upon the energy. These properties are in strongest contrast in the second period (Li to Ne) where the two sub-groups differ most in shape, and the contrast becomes progressively

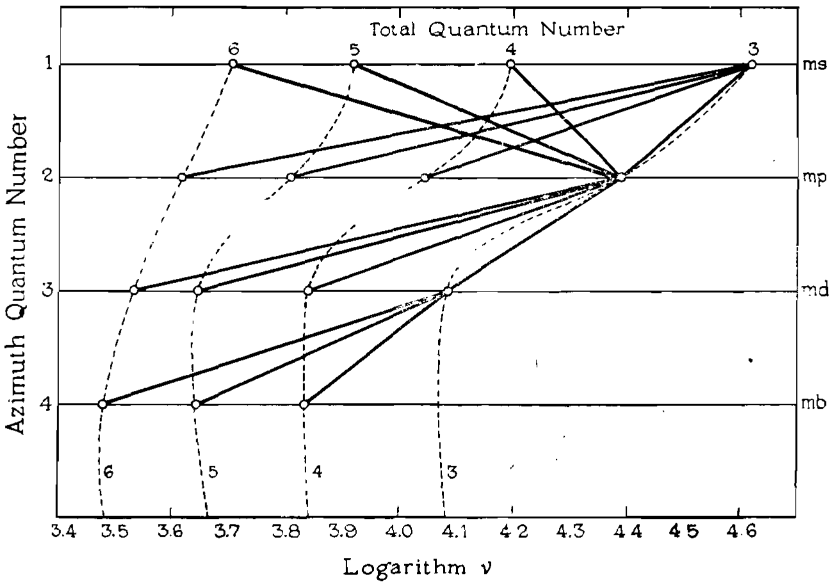


FIG. 46. Grotrian diagram for sodium on the basis of Bohr's new assignment of quantum numbers.

less in the following periods. Thus in the row starting with silver the two types of orbits 5_1 and 5_2 are only slightly different in shape and the chemical differences are likewise less pronounced.

In the long periods where changes occur in the sub-structure and not in the superficial groups we have successive elements with very similar physical and chemical properties. It is impossible to present in this outline a detailed consideration of the correspondence between properties of elements and the proposed models. Bohr attempts no explanation of the processes of chemical combination or crystal formation.

TABLE L

QUANTUM NUMBERS OF SERIES TERMS

Series Term	Sommerfeld Theory		Bohr Theory									
			Li arc		Na arc[1]		K arc[2]		Rb arc[3]		Cs arc[4]	
	n_a	n_r	n_a	n_r	n_a	n_r	n_a	n_r	n_a	n_r	n_a	n_r
1 *s*.......	1	0	1	1	1	2	1	3	1	4	1	5
2 *s*.......	1	1	1	2	1	3	1	4	1	5	1	6
3 *s*.......	1	2	1	3	1	4	1	5	1	6	1	7
2 *p*......	2	0	2	0	2	1	2	2	2	3	2	4
3 *p*......	2	1	2	1	2	2	2	3	2	4	2	5
4 *p*......	2	2	2	2	2	3	2	4	2	5	2	6
3 *d*......	3	0	3	0	3	0	3	1	3	2	3	3
4 *d*......	3	1	3	1	3	1	3	2	3	3	3	4
5 *d*......	3	2	3	2	3	2	3	3	3	4	3	5
4 *b*.......	4	0	4	0	4	0	4	0	4	1	4	2
5 *b*.......	4	1	4	1	4	1	4	1	4	2	4	3
6 *b*.......	4	2	4	2	4	2	4	2	4	3	4	4

[1] Similar numbers for Mg arc and spark.
[2] Similar numbers for Cu arc and Ca and Zn arc and spark.
[3] Similar numbers for Ag arc and Sr and Cd arc and spark.
[4] Similar numbers for Au arc and Ba and Hg arc and spark.

Arc and Spark Spectra. — A mathematical computation of the two orbits of normal helium and of the stages in the binding of the second electron is being worked out by Kramers and Bohr. The solution of this very difficult three body problem has, we are assured, already reached a stage that justifies the basic assumptions of the theory of non-hydrogen types of atom. In heavier elements a *rigorous* mathematical solution of the problem of the binding of the last electron offers difficulties that are apparently insurmountable. The choice of quantum numbers assigned to the normal state (1 *S*) by the Bohr theory makes it necessary to reject entirely Sommerfeld's theoretical computation of spectral series formulae. Table L indicates the system of quantum numbers assigned by Bohr to different series terms of elements in the first and second columns of the periodic table. For comparison we include in the table the numbers required by the Sommerfeld theory. It is noted that the azimuth numbers remain the same in the two theories. The inter-orbital transitions involved in arc spectra of sodium on the new Bohr hypothesis are shown in Figure 46. This should be

compared with Figure 9, which is based on the other theory. In Figure 46 the double p terms and transitions involving combination lines have been omitted for the sake of simplicity. By our choice of coördinates in these diagrams points and lines remain identical for the two theories, but total quantum numbers are entirely different. Hence the explanation of the features of Figure 9 applies, with the above noted exceptions, to Figure 46, although the mathematical expression for the variable term in a series formula would be entirely different. On the Bohr theory total quantum numbers characterizing these series will differ for elements of the same family, as shown in Table L.

Though a quantitative test of the Bohr theory of spectra is impossible for heavy elements because of the mathematics involved, yet a comparison of the relative magnitudes of different series limits in the same element, and of corresponding limits in different elements, offers a means of testing many of the assumptions as to the relative stability of the different types of orbit. For the elements preceding and following the long periods such comparisons are particularly interesting, but the subject is too complicated for treatment here.

Conclusion. — Bohr's new hypothesis of atomic structure was developed primarily from considerations of atomic stability, and is thus in marked contrast to other theories which in general postulate arbitrary configurations suitable for the explanation of a limited range of physical phenomena. It has been seen that in the field of x-ray spectra we find a striking confirmation of Bohr's assumptions as to the types of orbit appearing in the inner atom structure. It is only in the assumed space configurations of these orbits and in the superficial structure (Table XLIX) that the new theory can be open to question.

A space configuration of electrons is apparently essential for the explanation of chemical and physical phenomena other than radiation. The coplanar ring model assumed in the past for the mathematical computation of spectral frequencies was adopted because of its simplicity and was generally looked upon merely as an approximation to actual electron configurations. It has been applied with apparent success to a wide range of phenomena, notably, the theoretical derivation of the Ritz formula and the computation of x-ray frequencies.

The new Bohr theory apparently rejects this model even as an approximation, and the success of the theoretical deductions based on ring configurations offers the chief objection to the acceptance of the new viewpoint. In estimating the weight of this objection we must remember that the different applications of the ring model involve

many assumptions which are mutually inconsistent. The new theory avoids the artificiality inherent in other models but as a consequence it lacks the simplicity required for a direct mathematical test of its validity. Thus we can foresee that the quantitative verification of the details of this scheme of electron distribution may not be accomplished in the near future. At the present writing the entire subject is in the most elementary qualitative stage, but we are promised information of more quantitative natur

INDEX OF SUBJECTS

Absorption lines, Chapter IV, 78–108.
— —, of excited atoms, 93.
— —, of ionized atoms, 103.
— —, of normal atoms, 78.
— —, of subordinate series, 97.
— —, relation to critical potentials, 63.
Absorption phenomena, *see* x-rays.
Affinity for electrons, 177, 179.
— —, of excited argon, sodium and mercury, 106.
— —, of excited helium, 105.
— —, of hydrogen molecule, 76.
Aluminum.
—, *K* and *L* limits of, 204.
—, raies ultimes of, 143.
—, soft x-rays of, 195, 204.
Antimony.
—, raies ultimes of, 144.
—, resonance and ionization potentials of, 66.
Arc spectra, 111, 119.
— — and spark spectra of elements, 42.
— —, notation on basis of Bohr's new theory, 239.
— — of alkalis, 34.
— — of heavy atoms, 32–36.
— — of helium, 69.
— — of hydrogen, 17.
— — of metals of Group I, 134.
— — of metals of Group II, 125.
Arcs.
—, below ionization potential, 73, 77; 115, 153.
—, for determination of critical potentials, 116.
—, in nonatomic hydrogen, 77.
—, in sodium, of high luminous efficiency, 114.
—, intensity of emission proportional to current, 129.
—, reversals, 82.
Argon.
—, *M* limit, 212.
—, negative ion, 106.
—, resonance and ionization potentials of, 68.
Arsenic.
—, raies ultimes of, 143.
Arsenic, resonance and ionization potentials of, 66.
Aspherical nucleus, 28.
Atomic numbers of elements, 231.
Atomic structure, 15.
— —, atoms with many electrons, 30, 31.
— —, Bohr's new theory of, 232–241.
— —, hydrogen, 16, 74.
— —, ionized helium, 16.
— —, normal helium atom, 70.

Balmer series, 17, 22, 25, 28.
— —, absorption of, 97, 98.
— —, fine structure of, 25, 28, 37, 59, 76.
Band spectra, 105.
— —, continuous band in iodine, 178.
— —, of helium, 106.
— —, of mercury chlorides, 185.
— —, of nitrogen, 190.
— —, relation to critical potentials, 190.
Barium.
—, absorption of enhanced lines, 103.
—, development of spectrum, 125.
—, fundamental wave numbers of, 64, 85.
—, raies ultimes of, 142.
—, resonance and ionization potentials of, 64.
—, reversal of series $1S-ml$
—, series in, 44.
—, thermal ionization, 163, 170.
Beryllium.
—, resonance and ionization potentials of, 64.
—, soft x-rays of, 195.
Bismuth.
—, raies ultimes of, 144.
—, resonance and ionization potentials of, 66.
Boron.
—, *K* limit, 204.
—, soft x-rays of, 195.
Broadening of spectral lines, 27, 91.
Bromine.
—, critical potential of, 67.
—, electron affinity of, 179, 182, 186.
—, heat of dissociation of, 182, 186.
—, *K* absorption band, 196.

Cadmium.
—, absorption of λ 3260 and λ 2288 A, 81.

Cadmium, development of spectrum, 125.
—, fundamental wave numbers of, 64, 85.
—, raies ultimes of, 142.
—, resonance and ionization potentials of, 64.
—, series in, 44.
—, single line spectrum, 124.
—, thermal ionization, 163.
—, two line spectrum, 124.
Caesium.
—, absorption lines of, 80.
—, development of spectrum, 134.
—, fundamental wave numbers of, 62.
—, photo-electric effect in vapor, 217.
—, possibility of higher resonance potentials, 127.
—, raies ultimes of, 142.
—, resonance and ionization potentials of, 62.
—, reversal of subordinate series of, 108.
—, reversed lines, 82.
—, series in, 44.
—, single-doublet and arc spectra, 129.
—, thermal ionization of, 163.
Calcium.
—, absorption of λ 4227 A in furnace spectra, 82.
—, development of spectrum, 125.
—, flame spectrum, 166.
—, fundamental wave numbers of, 64, 84.
—, in solar spectrum, 171, 172.
—, in stellar spectra, 174.
—, raies ultimes of, 142.
—, resonance and ionization potentials of, 64.
—, reversal of enhanced lines, 103.
—, reversal of series 1 *S–mP*, 83.
—, series in, 44.
—, thermal ionization of, 160, 163, 170.
Carbon.
—, ionization and resonance potentials of compounds of, 188.
—, *K* limit, 204.
—, raies ultimes of, 143.
—, soft x-rays of, 195.
Chlorine.
—, critical potentials of, 67.
—, electron affinity of, 179, 182, **186**.
—, heat of dissociation of, 182, **186**.
—, soft x-rays of, 195.
Chromium.
—, in solar spectrum, 172.
—, raies ultimes of, 144.
Cobalt.
—, in solar spectrum, 172.
—, raies ultimes of, 144.
Columbium.
—, raies ultimes of, 143.
Copper.
—, development of spectrum of, **134**.
Copper, fundamental wave numbers of, 62.
—, ionization and resonance potentials of, 62.
—, raies ultimes of, 142.
—, reversal of λ 3248 and λ 3275 A, 83.
—, series in, 44.
—, soft x-rays of, 195.
—, thermal ionization of, 163.
Cumulative ionization, 148–156.

Data, numerical, 227–231.
Displacement law for spectra, 42.
Dissociation.
— of halogens, 182.
— of hydrogen, 75, 76.
Doppler-Fizeau effect, 27, 88, 91.

e/m, value of, 18.
Emission lines, Chapter V, 109–147.
— —, metals of Group I, 127.
— —, metals of Group II, 118.
— —, rare gases, 133.
Energy diagrams.
— —, Grotrian diagram; for hydrogen, 57; sodium, 58, 238.
— —, helium, 70.
— —, hydrogen, 52.
— —, ionized magnesium, 56.
— —, magnesium, 54.
— —, mercury, 101.
— —, sodium, 53, 58.
— —, sodium (Bohr's new theory), 238.
— —, tungsten (x-rays), 206.
— —, uranium (x-rays), 208.
Enhanced spectra, 113. (*See also* Spark spectra.)
— — constants in series formulae, 40.
— — of metals of Group I, 134.
— — of metals of Group II, 119, 125.
— —, relation between a^* and a, 41.
— —, relation between 1 𝔖 and 1 *S*, 124.
— —, series notation for, 41.
Excited atoms, 79, 90, 150.
— —, electron affinity of, 105.
— —, life of, 92, 93.
— —, line absorption spectra of, 93–108.
— —, produced thermally, 157–176.

Fine structure, 25, 26, 27.
— —, doublets and triplets, 37.
— —, *L*-doublet separation, 49.
— — of Balmer lines, 37.
— — of x-ray spectra, 209–213.
— —, relation of *L*-doublets to arc spectrum of neon, 136.
Flame spectra, 82, 84, 165.
— —, suppression of sodium lines with excess of chlorine, 184.
Fluorescence, 90, 107.

Fluorescence, of mercury, 104, 107.
— of x-radiation, 197.

Gallium.
—, raies ultimes of, 143.
Germanium.
—, raies ultimes of, 143.
Gold.
—, development of spectrum of, 134.
—, fundamental wave numbers of, 62.
—, *N*-limit, 204.
—, raies ultimes of, 142.
—, resonance and ionization potentials of, 62.
—, reversal of λ 2428 A, 83.
—, series in, 44, 83.
—, thermal ionization of, 163.
Grating energy, 179.
— — of alkali halides, 182.
— — of ZnS, 183.

h, determinations of, involving line spectra, 223–226.
Helium.
—, absorption of excited atom, 103.
—, compounds of, 74, 106.
—, development of spectrum of, 133.
—, electron affinity of, 105.
—, energy diagram, 70.
—, fine structure of ionized, 28.
—, in stellar spectra, 174.
—, *K* series, 199.
—, metastable, 73.
—, new ultra-violet lines, 77.
—, ortho- and par-helium, 72.
—, photo-electric effect in, 222.
—, resonance and ionization potentials of, 68, 73.
—, resonance radiation of, 90.
—, series in ionized atom, 17.
—, series in neutral atom, 69–74.
—, structure of ionized atom, 16.
—, the normal atom, 69.
Hydrogen.
—, arcs in, 77.
—, continuous absorption in, 222.
—, doublet separation, 29.
—, electron affinity of molecule, 76.
—, energy diagrams, 52, 57.
—, halides, ionization potentials of, 186, 188.
—, in solar spectrum, 171.
—, in stellar spectra, 174.
—, ionization potential of HCN, 188; of water vapor, 188.
—, life of excited atom, 96.
—, molecule, 74–77.
—, ratio of mass of nucleus and atom to mass of electron, 18.
Hydrogen, resonance and ionization potentials of, 68.
—, series in, 17, 22.
—, structure of atom, 16.
—, sulphide, ionization of, 187.
—, thermal ionization of, 161, 163.
—, work of dissociation of, 75, 76.

Impact damping, 92.
Indium.
—, raies ultimes of, 143.
Iodine.
—, electron affinity, 179, 182, 186.
—, emission from recombination, 190.
—, emission spectrum, 178.
—, heat of dissociation, 182, 186.
—, resonance and ionization potentials of, 67.
Ionization. (*See also* Ionization potentials.)
— by photo-electric action, 154, 217.
— by photo-impact, 148.
— by successive impact, 148.
Ionization potentials.
— —, determination of *h*, 225.
— —, higher, and x-ray limits, 196.
— —, of compounds, 179–191.
— —, of elements, 60–68.
Iridium.
—, raies ultimes of, 144.
Iron.
—, in solar spectrum, 172.
—, raies ultimes of, 144.
—, soft x-rays, 195.

Lead.
—, raies ultimes of, 143.
—, resonance and ionization potentials of, 65.
Life of excited atoms, 92, 105.
— —, measurement of, 93.
Limits of series.
— — arc spectra, 125, 134.
— — enhanced spectra, 118, 125, 134.
— — significance of x-ray, 209.
— — spectral, 45; determining ionization, 61, 111, 112.
— — x-ray, 46, 195, 198, 201, 203, 204.
Lithium.
—, absorption lines of, 80.
—, development of spectrum of, 134.
—, doubly ionized, 16, 42; series in, 44.
—, flame spectrum, 166.
—, fundamental wave numbers of, 62.
—, ionization and resonance potentials of, 62.
—, raies ultimes of, 142.
—, reversed lines, 82.
—, thermal excitation of, 168.
—, thermal ionization of, 163.

Long lines, 141.
Lyman series, 17, 25, 59, 75.

Magnesium.
—, absorption of enhanced lines, 103.
—, absorption of λ 2852 and λ 2026 A, 82.
—, complete arc spectrum, 121
—, complete enhanced spectrum, 122.
—, development of spectrum, 118, 125.
—, energy diagrams, 54, 56.
—, fundamental wave numbers of, 64, 84.
—, in stellar spectra, 174.
—, raies ultimes of, 142.
—, resonance and ionization potentials of, 64.
—, series in, 44.
—, single line spectrum, 118.
—, single line spectrum of ionized, 122.
—, soft x-rays, 195, 204.
—, thermal ionization, 163.
—, two line spectrum, 121.
Manganese.
—, in solar spectrum, 172.
—, raies ultimes of, 144.
—, 1 *S* and ionization potential, 67.
Mass.
—, correction for finite, of nucleus, 17.
—, of hydrogen nucleus, 15.
—, ratio of, hydrogen nucleus and atom to mass of electron, 18.
Mercury.
—, absorption coefficient of vapor for resonance radiation, 89.
—, absorption of subordinate series, 99,
—, absorption of λ 1849 and λ 2537 A. 81, 88, 89, 100, 108.
—, development of spectrum of, 125.
—, energy diagram, 101.
—, fluorescence, 104.
—, fundamental wave numbers of, 64, 85.
—, higher critical potentials, 137.
—, ionization potential of $HgCl_2$, 188.
—, metastable form of, 102, 106, 108, 140.
—, molecule, 106.
—, raies ultimes of, 143.
—, resonance and ionization potentials of, 64.
—, resonance potential by probe wire measurements, 114.
—, resonance radiation, 86–89.
—, series in, 44.
—, single line spectrum, 124.
—, thermal ionization, 163.
Molybdenum.
—, raies ultimes of, 144.
—, soft x-rays, 195.

Neon.
—, development of spectrum, **136.**
Neon, *L* series, 200.
—, resonance and ionization potentials of, 68.
Nickel.
—, in solar spectrum, 172.
—, raies ultimes of, 144.
—, soft x-rays, 195.
Nitrogen.
—, complex critical potentials, 190.
—, excitation of band spectra, 190.
—, resonance and ionization potentials of, 66.
—, soft x-rays, 195.
Nuclear defect of a ring of electrons, 37, 227.
Numerical magnitudes, 228.

Orbits, 15.
—, application of general quantizing equation, 21.
—, circular, of hydrogen and ionized helium, 16, 23.
—, elliptical, 19, 21.
—, modifications arising in relativity considerations, 24.
—, of helium, 70.
Oxygen.
—, resonance and ionization potentials of, 67.
—, soft x-rays, 195.

Palladium.
—, raies ultimes of, 144.
Paschen series, 17, 25, 59.
Periodic table, 30, 231.
Phosphorus.
—, raies ultimes of, 143.
—, resonance and ionization potentials of, 66.
—, soft x-rays, 195.
Photo-electric effect in vapors, 216–222.
— — and ionization, 217.
— — in caesium vapor, 217.
Photo-electric ionization, 148.
Platinum.
—, raies ultimes of, 144.
Potassium.
—, absorption lines of, 80.
—, continuous absorption, 221.
—, development of spectrum of, 134.
—, fundamental wave numbers of, 62.
—, heat of sublimation of, 182.
—, ionization and resonance potentials of, 62.
—, raies ultimes of, 142.
—, reversed lines, 82.
—, reversal of subordinate series of, 108.
—, series in, 44.
—, single line, arc, and enhanced spectra, 129.

Potassium, thermal ionization of, 163.
—, soft x-rays, 195.

Quantum numbers, 16.
— —, definition of azimuthal and radial, 21.
— —, determination of, 20.
— —, for alkalis, 34.
— —, for hydrogen series, 17.
— —, of series terms on basis of Bohr's new theory, 239.
— —, of x-ray limits, 210.
Quantum theory, 15–50.

Radium.
—, development of spectrum of, 125.
—, fundamental wave numbers of, 64.
—, resonance and ionization potentials of, 64.
—, series in, 44.
Raies ultimes, 141.
— — of the elements (table), 142.
Relativity, of mass, 24.
— — hydrogen doublet, 29.
— — L-doublet, 49.
Resonance potentials.
— —, determination of h, 225.
— —, of compounds, 188.
— —, of elements, 60–68.
Resonance radiation, 86, 147.
Retarded potential, 28.
Reversed lines, 82.
Rhodium.
—, raies ultimes of, 144.
Ritz equation, 32, 43.
Rubidium.
—, absorption lines of, 80.
—, development of spectrum of, 134.
—, fundamental wave numbers of, 62.
—, raies ultimes of, 142.
—, resonance and ionization potentials of, 62.
—, reversal of subordinate series, 108.
—, reversed lines, 82.
—, series in, 44.
—, thermal ionization of, 163.
Ruthenium.
—, raies ultimes of, 144.
Rydberg number, N, N_∞, N_H, N_{He}, 17, 18, 19.
— —, determination of h, 224.

Scandium.
—, in solar spectrum, 172.
—, raies ultimes of, 143.
Selection, principle of, 26, 28, 35, **72, 86,** 87, 88, 121, 140.
— — in absorption, 78.
— — in x-rays, 212.
Selection, principle of, representation in Grotrian diagrams, 59.
— —, $1s$–$3d$ in sodium and potassium, 130.
Selenium.
—, resonance and ionization potentials of, 67.
Series. (*See* x-rays.)
—, absorption, Chapter IV.
—, emission, Chapter V.
—, graphic representation of, 51–59.
—, in alkalis, 34.
—, in heavy atoms, 32–36.
—, in helium, 17.
—, in hydrogen, 17.
—, lines correlated with temperature, 169.
—, notation and formulae, 43–46.
—, notation on basis of Bohr's new theory, 239.
—, reversals, 82.
Silicon.
—, raies ultimes of, 143.
—, soft x-rays, 195.
Silver.
—, development of spectrum, 134.
—, fundamental wave numbers of, 62.
—, K absorption band, 196.
—, raies ultimes of, 142.
—, resonance and ionization potential of, 62.
—, series in, 44.
—, thermal ionization of, 163.
Size.
— of hydrogen nucleus, 15.
— radius of hydrogen atom, 38.
Sodium.
—, absorption of, 79.
—, continuous absorption of, 219, 220.
—, energy diagrams, 53, 58.
—, development of spectra of, 129, 134
—, energy diagram (Bohr's new theory) 238.
—, flame spectrum, 166.
—, fundamental wave numbers of, 62, 87
—, in solar spectrum, 171, 172.
—, ionization and resonance potential of, 62.
—, metastable ion, 130.
—, negative ion, 106.
—, raies ultimes of, 142.
—, resonance radiation, 86.
—, reversal of subordinate series, 97, 108
—, reversed lines, 82.
—, series in, 44.
—, single line spectrum, 129.
—, soft x-rays, 195, 204.
—, subordinate series terms of highe order, 117.
—, thermal excitation, 165.

Sodium, thermal ionization, 163.
Solar spectra, 169, 170.
Spark spectra, 39, 112.
— —, alkali earths, 118.
— —, helium, 17, 28.
— —, notation on basis of Bohr's new theory, 239.
Spectroscopic analysis, 141.
Spectroscopic tables, 43.
Stark effect, 7, 27, 29.
Stellar.
—, continuous band absorption in spectra, 222.
— spectra, 169, 172, 174, 176.
— temperatures, 173, 176.
Stokes' law, 102.
Strontium.
—, absorption of enhanced lines, 103.
—, development of spectrum, 125.
—, flame spectrum, 166.
—, fundamental wave numbers of, 64, 85.
—, in solar spectrum, 172.
—, raies ultimes of, 142.
—, resonance and ionization potentials of, 64.
—, reversal of series 1 *S–mP*, 83.
—, series in, 44.
—, thermal ionization of, 163, 170.
Sulphur.
—, electron affinity of, 179, 183.
—, heat of dissociation of, 183.
—, heat of sublimation of, 183.
—, resonance and ionization potentials of, 67.
—, soft x-rays, 195.

Tantalum.
—, raies ultimes of, 143.
Tellurium.
—, raies ultimes of, 144.
—, resonance and ionization potentials of, 67.
Thallium.
—, absorption of vapor, 83.
—, excitation of lines of, in mixtures of Tl and Hg, 108.
—, raies ultimes of, 143.
—, resonance and ionization potentials of, 65.
—, reversals in arc, 83.
Thermal excitation, 157–176.
Thermochemical relations, 177–191.
Thermodynamics of excitation and ionization, 157–176.
Tin.
—, raies ultimes of, 143.
Titanium.
—, in solar spectrum, 172.
—, raies ultimes of, 143.
—, soft x-rays, 195.
Tungsten.
—, complete x-ray spectra of, 205–207.
—, energy diagram (x-rays), 206.
—, raies ultimes of, 144.
—, soft x-rays, 195.

Ultra-violet, continuous source of, 81.
Uranium.
—, energy levels (x-rays), 208.
—, *K* limit, 199.

Vanadium.
—, in solar spectrum, 172.
—, raies ultimes of, 143.
Velocities of electrons, ions and molecules, 229.

Wave number, definition of, 17.

X-rays, 46–50, 192–215.
—, absorption limits (table), 204.
—, absorption phenomena, 196.
—, combination principle, 204.
—, critical potentials for excitation, 193.
—, determination of *h*, 223.
—, diagram of *K* limits, 201.
—, diagram of *L* and *M* limits, 203.
—, diagram of x-ray limits of elements, 198.
—, emission lines, 204.
—, interpretation by Bohr's new theory, 237.
—, *N* series, 215.
—, relation to arc spectrum of neon, 136.
—, significance of limits, 209.
—, simple series nomenclature, 47.
—, spark lines accompanying, 134.
—, structure of band absorption, 200.
—, table of soft x-rays, 195.
—, values of ν/N, 48.

Yttrium.
—, raies ultimes of, 143.

Zeeman effect, 7, 29.
Zinc.
—, absorption of λ 3076 and λ 2139 A, 82.
—, development of spectrum of, 125.
—, fundamental wave numbers of, 64, 84.
—, heat of sublimation of, 183.
—, ionization potentials of $ZnCl_2$ and zinc ethyl, 187, 188.
—, raies ultimes of, 142.
— resonance and ionization potentials of, 64.
—, series in, 44.
—, single line and two line spectra, 124.
—, thermal ionization of, 163.
Zirconium.
—, raies ultimes of, 143.

INDEX OF AUTHORS

Adams, Edwin Plimpton, 50.
Anderson, J. A., 72.

Bazzoni, C. B., 195, 213, 214.
Bergengren, J., 215.
Bevan, P. V., 80.
van der Bijl, H. J., 155.
Birge, R. T., 19, 190, 223.
Bloch, E., 190.
Bloch, Leon, 190.
Bodenstein, M., 186.
Bohr, Nils, 7, 16, 26, 28, 30, 31, **35**, **36**, 50, 69, 71, 74, 77, 130, 186, 214, **215**, 232–241.
Bormann, Elisabeth, 183, 186.
Born, Max, 179, 183, 186.
Boucher, P. E., 188.
Brackett, F. S., 135.
Bragg, W. H., 204.
Brandt, Erich, 66, 190.
de Broglie, M., 192 B, 197, **199**, **214**, **215**.
Budde, Hans, 183.

Cario, 108.
Catalan, M., 67.
Child, C. D., 156.
Chi-Sun-Yeh, 223.
Clark, H., 224.
Coblentz, W. W., 172, 173.
Compton, K. T., 8, 67, 68, 135, 148, 151, 153, 168, 189.
Coster, D., 205, 215.
Curtiss, R. H., 97.

Darwin, C. G., 28.
Dauvillier, A., 215.
Davies, A. C., 67, 68, 75, 95, 136, 222.
Davis, Bergen, 137.
Dempster, A. J., 96.
Dixon, A. A., 67.
Dolejsek, V., 215.
Duane, William, 197, 199, 205, 212, 215, 223, 224.
Duffenback, O. S., 77.
Dunoyer, L., 87.
Dunz, Berthold, 43.
Dushman, Saul, 26.

Edwards, E., 81, 137.
Einsporn, E., 120, 137.
Einstein, A., 197.

Fairchild, C. O., 99.
Fajans, K., 182.
Foote, Paul D., 36, 60–68, 75, 76, 81, 108, 116, 118, 124, 128, 129, 130, 132, 186, 187, 188, 190, 194, 195, 200, 201, 204, 213, 214, 217, 225.
Fortrat, R., 79.
Fowler, A., 39, 43–46, 50, 64, 65, 66, 67, 69, 136.
Franck, J., 7, 68, 71, 73, 74, 77, 90, 91, 92, 105, 106, 108, 120, 124, 133, 137, 177, 183, 186.
Fricke, Hugo, 72, 199, 200, 204, 215.
Fuchtbauer, Chr., 100, 155, 217.

Gehrcke, E., 28.
Gerlach, W., 77, 183.
Gossling, B. G., 188.
Goucher, F. S., 137.
de Gramont, A., 141.
Grotrian, Walter, 59, 105, 106, **114**, **136**, 138, 239.
Guthrie, D. V., 81, 83.

Harrison, G. R., 80, 219.
Hartley, W. N., 141.
Hartmann, J., 222.
Henderson, J. P., 124.
Hertz, G., 124, 199, 215.
Hicks, W. M., 45.
Hjalmar, E., 215.
Holden, W. H., 230.
Holtsmark, J., 220.
Holweck, F., 202, 204, 215, 224.
Horton, Frank, 67, 68, 75, 95, 136, 2[illegible]
Howe, H. E., 81.
Hoyt, F. C., 205, 214.
Huggins, William, 222.
Hughes, A. L., 66, 67, 68, 77, 195, [illegible] 214, 216.
Hulburt, E., 81.
Hull, A. W., 224.

Ireton, H. J. C., 124.

Jolly, H. L. P., 129.

Kannenstine, F. M., 73.
Kayser, H., 97, 103.
Kemble, E. C., 70, 74.
Kiess, C. C., 141.

King, A. S., 82, 103, 108, 169, 170.
Klein, O., 108.
Knipping, P., 68, 71, 73, 133, 186, 188.
Konen, H. M., 43.
Kossel, W., 42, 200, 205, 215.
Kramers, H. A., 29, 239.
Kunz, J., 217.
Kurth, E. H., 76, 194, 195, 204, 213, 214.

Ladenburg, R., 99, 223.
Lande, A., 71.
Langmuir, Irving, 30, 75, 152, 186.
Lau, F., 28.
Lenz, W., 106, 190.
Lewis, E. P., 81.
Lewis, G. N., 30.
Lilly, E. G., 135.
Lindh, A. E., 215.
Lockyer, Norman, 141.
Lohmeyer, J., 185.
Lorenser, E. D., 43.
Lorentz, H. A., 91, 92.
Lowe, P., 28.
Lyman, Theodore, 72, 77.

McLennan, J. C., 8, 28, 77, 81, 82, 83, 124, 137, 165.
Mees, C. E. K., 129.
Merton, T. R., 28.
Meggers, W. F., 8, 36, 81, 82, 85, 97, 108, 116, 118, 124, 128, 129, 130, 132, 141, 142, 166, 190.
Metcalfe, E. P., 99.
Mie, Gustav, 96.
Millikan, R. A., 204, 213, 215.
Milne, E. A., 171.
Mixter, W. G., 183.
Mohler, F. L., 36, 62–68, 75, 76, 81, 87, 108, 116, 118, 124, 129, 130, 132, 186, 187, 188, 190, 194, 195, 200, 201, 204, 213, 214, 217, 235.
Moseley, J. H., 192, 204.
Munch, W., 172.

Nagaoka, H., 27.
Noyes, A. A., 8.
Noyes, W. A., 8.

Oldenberg, O., 28.

Page, Leigh, 50.
Palmer, H. H., 223.
Paschen, F., 7, 18, 19, **28, 29, 30, 43, 65**, 73, 103, 136, 225.
Peters, C. G., 85.
Phillips, F. S., 104.
Pier, M., 186.
Planck, M., 16, 24, 223.
Pollitzer, F., 183.

Raleigh, Lord, 24, 91.
Randall, H. M., 65.
Rawlinson, W. F., 214.
Reiche, F., 71, 73, 74.
Rice, M., 224.
Richardson, O. W., 195, 213, **214.**
Robinson, H., 214.
Ross, P. A., 214.
Rosseland, S., 108.
Ruark, Arthur E., 8, 28, 230.
Rubinowicz, A., 26, 36, 212.
Russell, H. N., 171, 172, 175.
Rutherford, Ernest, 15, 197, 214.

Saha, M. N., 67, 159, 171, 172, 173, 175.
Saunders, F. A., 84, 85.
Scheiner, J., 172, 173.
Siegbahn, M., 205, 208 A, 208 B, 215.
Silberstein, Ludwick, 28, 50.
Skinner, C. A., 8.
Smekal, A., 205, 215.
Smyth, H. D., 67, 189.
Sommerfeld, A., 7, 20, 24, 26, 28, 32, 36, 40, 42, 49, 50, 62, 120, 140, 190, 209, 210, 215.
Starck, G., 186.
Stark, J., 153.
Stead, G., 188.
Stenstrom, W., 199, 200, 215.
Steubing, W., 178.
Stimson, F. J., 141.
Stratton, S. W., 8.
Strutt, R. J., 86.

Tate, J. T., 60, 63.
Thomson, A., 165.
Tolman, R. C., 8, 157, 158, **164.**

Udden, A. D., 67.

Van Vleck, J. H., 74.
Venkatesachar, B., 99.
Vinal, G. W., 18.

Waidner, C. W., 8.
Webster, D. L., 194, 214, 244.
Wentzel, G., 205, 212, 215.
Wien, W., 96.
Williams, E. H., 217.
Wilsing, J., 172, 173.
Wilson, W., 20.
Wood, R. W., 79, 80, 81, 83, 86, 87, 88, 89, 96, 98, 105, 107, 152, 168, 190, 218, 219.
Wooten, B. A., 224.

Young, J. F. T., 83.

Zahn, H., 98, 166, 167.

...ULTURAL COLLEGE AND ... LIBRARY
No. 1228
10 JUN 1924